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US-A-4 406 779

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Description

The present invention relates to a single-stage hydrorefining process for treating heavy oils using catalysts arranged in a particular manner, referenced to herein as "stacked bed". It particularly relates to a single-stage hydrorefining process for treating oils having a tendency to deactivate hydrotreating catalysts by coke formation, these being oils with high boiling components and/or oils with a low asphaltene content and very high boiling components, with a particular stacked bed catalyst arrangement. It has been found that the use of a stacked bed increases the catalyst life or allows increased conversions relative to the more traditional catalysts used for the treating of these oils. The invention is particularly useful for meeting the demands of increasing hydrotreatment severity, such as sulphur removal, for poorer quality heavy oil fractions both directly distilled or extracted from crude or crude fraction and oil fractions from thermal, steam, or catalytic cracking processes including mixtures of any of these materials.

The continual changes in the refining industry such as the trend to poorer quality crudes and the continual increase in the stringency of oil product specifications (e.g. lower allowed sulphur content) is in part requiring the refiner to increase the severity of hydrotreating of traditional oil fractions and/or process fractions not traditionally treated. The increased severity and/or unusual feed generally have been causing increased deactivation of hydrotreating catalysts. By using the process according to the present invention the run length of a hydrotreating process with these oil fractions can be increased and/or higher severity operation and/or processing poorer quality oils can be allowed.

The use of lower price or locally available crudes frequently results in increased sulphur and/or nitrogen content of the oil fractions. Conversion processes such as thermal cracking, coking and catalytic cracking are either being brought on-stream or are already processing poorer quality oils. The products from such processes are laden with heteroatoms such as sulphur and are more hydrogen deficient relative to products from better quality crudes or oils distilled directly from crude or crude fractions. As a result, the products of the conversion processes and/or poorer crudes have to be additionally hydrotreated to meet specifications or to prepare for further treating/conversion. However, the higher operating temperatures required to remove the additional heteroatoms and adding additional hydrogen in addition to the hydrogen-deficient coke-like nature of these feeds result in increasing deactivation of the hydrotreating catalysts due to coking. Any increase in hydrotreating catalyst activity and/or stability would enable refiners to upgrade the lower value poor quality and/or cracked oils at a significant economic benefit.

It is well known that hydrogen-deficient poor quality oils can be hydrotreated/hydrorefined with low catalyst deactivation rates at higher hydrorefining unit conditions—higher hydrogen pressure, and/or hydrogen-to-oil ratio, and/or oil-catalyst contact time. To stay within the physical or design constraints of a unit or to continue to process the required volumes of oil, only relatively small variations in these parameters can be made. As a result, very expensive hydrotreating equipment must be added to meet the changing goals unless catalysts with longer lives are available. Alternatively, the refiner has to accept very short catalyst lives and increased down time for frequent catalyst changes or use continuous or semicontinuous regeneration facilities. Larger and/or more vessels and additional equipment would be needed to process a given quantity of feedstock with these options. Of particular importance to a refiner is the ability to process the hydrogen-deficient and/or poorer quality oils in existing hydrotreating units which do not have sufficient hydrogen pressure to prevent uneconomically rapid catalyst activity loss with existing catalysts utilized in a non-stacked bed configuration. Thus, improved processes and highly stable catalysts are in great demand.

Several two-stage hydrotreating processes have been proposed in the art to overcome some of the difficulties of hydrotreating heavy oils. Reference is made to five patent specifications, wherein use is made of two catalyst reactor vessels.

In U.S. patent specification 3,766,058 a two-stage process is disclosed for hydrodesulphurizing high-sulphur vacuum residues. In the first stage some of the sulphur is removed and some hydrogenation of the feed occurs, preferably over a cobalt-molybdenum catalyst supported on a composite of ZnO and Al₂O₃. In the second stage the effluent is treated under conditions to provide hydrocracking and desulphurization of asphaltenes and large resin molecules contained in the feed, preferably over molybdenum supported on alumina or silica, wherein the second catalyst has a greater average pore diameter than the first catalyst.

In U.S. patent specification 4,016,069 a two-stage process is disclosed for hydrodesulphurizing metal- and sulphur-containing asphaltenic heavy oils with an interstage flashing step and with partial feed oil bypass around the first stage.

In U.S. patent specification 4,048,060 a two-stage hydrodesulphurization and hydrodemetallization process is disclosed wherein a different catalyst is utilized in each stage and wherein the second stage catalyst has a larger pore size than the first catalyst and a specific pore size distribution.

In U.S. patent specification 4,166,026 a two-step process is taught wherein a heavy hydrocarbon oil containing large amounts of asphaltenes and heavy metals is hydrodemetallized and selectively cracked in the first step over a catalyst which contains one or more catalytic metals supported on a carrier composed mainly of magnesium silicate. The effluent from the first step, with or without separation of hydrogen-rich gas, is contacted with hydrogen in the presence of a catalyst containing one or more catalytic metals supported on a carrier, preferably alumina or silica-alumina, having a particular pore volume and pore size

distribution. This two-step method is claimed to be more efficient than a conventional process wherein a residual oil is directly hydrodesulphurized in a one-step treatment.

In U.S. patent specification 4,392,945 a two-stage hydrotreating process for treating heavy oils containing certain types of organic sulphur compounds is disclosed wherein use is made of a specific sequence of catalysts with interstage removal of H_2S and NH_3 . A nickel-containing conventional hydrotreating catalyst is present in the first stage. A cobalt-containing conventional hydrotreating catalyst is present in the second stage. The first stage is preferably operated under conditions to effect at least 50%w desulphurization, while the second stage is preferably operated under conditions to achieve at least about 90%w desulphurization, relative to sulphur present in the initial oil feed to the first stage. This process is primarily applicable to distillate gas oil feeds boiling below 343°C which contains little or no heavy metals.

All of the patent specifications referred to hereinabove relate to two-stage hydrotreating processes for various hydrocarbon oils utilizing certain advantageous catalysts and/or supports. In some of these processes removal of H_2S and NH_3 is required. However, no reference is made in any of the afore-mentioned patent specifications to a process whereby oils with final boiling points from 343°C to 538°C and/or oil with a low asphaltene content and with components boiling above 538°C can be hydrotreated with significantly improved catalyst life relative to a single catalyst system. It has now been found that by using a specific stacked-bed catalyst arrangement containing different catalytically active compositions, oils with high boiling components (about 343°C—538°C and/or oils with a low asphaltene content and with very high boiling components (above 538°C) can be treated in a single stage hydrotreating process with improved catalyst-system life and/or increased hydrotreating conversions for a given feedstock. The process according to the present invention allows easy conversion of existing catalytic hydrotreating reactors to a stacked bed of specified catalysts. The present process operates well at hydrogen pressures below 75 bar (7500 kPa), so that no additional high pressure reactors need be constructed. The particular stacked bed combination of catalysts in accordance with the invention results in longer runs between replacements or regenerations for a given oil than would be experienced with either catalyst used alone. Alternatively, poorer quality oils can be processed at equivalent conversions or higher conversions for a given oil can be maintained with the same time between replacement or regeneration with the use of the single-stage stacked bed catalyst system according to the present invention. The invention can be applied most usefully in situations where rapid catalyst deactivation is occurring.

The present invention thus relates to a process for catalytically hydrotreating hydrocarbon oils at elevated temperature and pressure in the presence of hydrogen by passing:

- a) oils having a final boiling point greater than 538°C and containing less than 2%w of heptane asphaltenes,
- b) oils having a final boiling point from 343°C to 538°C, or
- c) mixtures thereof,

downwardly with hydrogen or a hydrogen-containing gas into a hydrotreating zone over a stacked-bed of hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to hydrogen sulphide; wherein said stacked-bed comprises an upper zone containing 15—85%v, based on total catalyst, of a hydrotreating catalyst comprising a component from Group VIB of the Periodic Table, a Group VIII metal or metal oxide or metal sulphide and a phosphorus oxide and/or sulphide, and a lower zone containing 15—85%v, based on total catalyst, of a hydrotreating catalyst comprising a component from Group VIB, a Group VIII metal or metal oxide or metal sulphide and less than 0.5%w of phosphorus; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having a reduced heteroatom content.

It should be noted that from U.S. patent specification 4,016,067 a process is known for catalytic demetallization and desulphurization using a reactor containing two beds of phosphorus-free catalysts, which each fulfil specific requirements as to surface area and pore size and which both comprise Group VIB and Group VIII-compounds.

The process according to the present invention is particularly suitable for systems where catalyst deactivation due to coking is a constraint. The bottom bed catalyst is preferably Ni-promoted when nitrogen removal is the predominant concern and is preferably Co-promoted when sulphur removal is the predominant concern.

According to the present invention oils having a) final boiling point above 538°C whilst having a heptane asphaltenes content less than about 2% by weight, b) final boiling points in the range between 343°C and 538°C, or c) mixtures thereof are contacted with hydrogen or a hydrogen-containing gas and passed downwardly under hydrodesulphurization conditions over a stacked-bed catalyst. The boiling points referred to in the present description are as defined by the American Society for Testing and Materials (ASTM) method D 2887—83 ("Boiling Range Distribution of Petroleum Fractions by Gas Chromatography") and is commonly known as TBP-GLC (true boiling point by gas liquid chromatography). Normal heptane asphaltenes (asphaltenes) as discussed herein are measured by the Institute of Petroleum, London, method IP 143/78 ("Asphaltenes Precipitation with Normal Heptane").

The oils to be used as feedstock in the process according to the present invention will be oils having a tendency to deactivate hydrotreating catalysts by coke formation, under hydrotreating conditions and particularly under hydrodesulphurization conditions.

Downwardly has been used in this specification to indicate a direction and not an orientation and hence should not be construed to imply an orientation limitation on the instant invention. A downwardly series flow of oil and gas through a reactor is the usual pattern; however, one could invert the reactor conceptually and put oil and gas in at the bottom in which the first catalyst zone (Ni- and P-containing catalyst) should be the first main catalyst contacted by the oil and gas and would thus be in the bottom of the first reactor. As is well known in the industry, multiple reactors connected in series are placed individually. Oil and gas out of one reactor is piped up to the top of the next reactor; however, this process could be inverted. The above-described reactor configurations, as well as others apparent to those skilled in the art, are deemed to be within the scope of this invention.

The feedstocks to be applied in the process in accordance with this invention may be taken from straight run oils (non-cracked) or thermally-, steam-, or catalytically cracked hydrocarbonaceous materials. Suitable feeds include petroleum derived gas oils distilled from crude or crude fractions at atmospheric or at reduced pressure; solvent extracted oils such as extracted oils commonly referred to as Deasphalted Oils; thermally or steamed cracked oils or fractions thereof such as coker gas oils; gas oils or cycle oils from catalytic cracking and mixtures of two or more of the above materials.

Multiple uses of these feedstocks after initial treating in accordance with the process according to the present invention are also possible. Depending on particular feedstocks treated, suitable uses may include feed and additions to feed to units for significant molecular weight reduction such as catalytic cracking units or hydrocracking units; direct use or by blending with other oils or additives for sale as transportation fuels such as diesel oils; or for refinery fuel.

The stacked-bed catalyst system to be used in the process according to the present invention comprises firstly a normally Ni- and P-containing conventional hydrotreating catalyst. The second catalyst to be contacted by the oil normally comprises a low- or no-phosphorus content conventional catalyst. Preferably, the second catalyst contains no phosphorus. The second catalyst is also a conventional catalyst and contains Ni and/or Co in the formulation. When desulphurization is the primary objective of the hydrotreating process, the second catalyst contains Co in preference to Ni; when denitrogenation is the primary objective, the second catalyst preferably contains Ni in preference to Co. The catalysts herein can be prepared by techniques well known in the art. The advantages of this invention primarily accrue from the particular combination of operable hydrotreating catalysts in a stacked-bed rather than from any particular method or manner of fabricating the catalyst.

The first main hydrotreating zone catalyst used in the process according to the present invention suitably comprises a Ni- and P-containing conventional hydrotreating catalyst. Conventional hydrotreating catalysts which are suitable for the first catalyst zone generally comprise a phosphorus oxide and/or sulphide component and a component, selected from group VIB of the Periodic Table and a group VIII metal or metal oxide, or metal sulphide and/or mixtures thereof composited with a support. These catalysts will contain up to 10%w, usually 1 to about 5%w of the group VIII metal compound calculated on the base of the metal content, from 3 to about 15%w of the group VIB metal compound calculated on the base of the metal content, and from 0.1 to 10%w phosphorus compounds calculated on the base of phosphorus content. Preferably, the catalyst comprises a nickel component and a molybdenum and/or tungsten component with an alumina support which may additionally contain silica. A more preferred catalyst comprises a nickel component, a molybdenum component, and a phosphorus component with an alumina support which may also contain small amounts of silica. Preferred amounts of components range from 2 to 4%w of a nickel component calculated on the base of metal content 8—15%w of a molybdenum component calculated on the base of metal content, and 1 to 4%w, more preferably 2 to 4%w, of a phosphorus component calculated on the base of the phosphorus content. The catalyst can be used in any of a variety of shapes such as spheres and extrudates. The preferred shape is a trilobal extrudate. Preferably, the catalyst is sulphided prior to use, as is well known to the art.

The use of low-phosphorus or no-phosphorus catalysts in the second zone is thought to be of benefit due to reduced deactivation by coking.

Low-phosphorus content catalysts having high surface areas (greater than about 200 m²/g) and high compacted bulk densities (0.6—0.85 g/cm³) are preferably used for the second zone as they appear to be highly active. The high surface area increases reaction rates due to generally increased dispersion of the active components. Higher density catalysts allow one to load a larger amount of active metals and promoter per reactor volume, a factor which is commercially important. The metal content specified above provides high activity per reactor volume. Lower metal contents normally result in catalysts exerting two low activities for proper use in the process according to the present invention. Higher metal loadings than specified above do not contribute significantly to the performance and thus lead to an inefficient use of the metals resulting in high catalyst cost with little advantage. Since deposits of coke are thought to cause the majority of the catalyst deactivation, fresh catalyst pore volume should be at or above a modest level (0.4—0.8 cm³/g, more narrowly 0.5—0.7 cm³/g). The second zone catalyst can be used like the first zone catalyst in a variety of shapes. Preferably, the catalyst is sulphided prior to use as is well known to the art.

The Ni-containing catalyst used for the first zone is preferably a high activity conventional catalyst suitable for high levels of hydrogenation. Such catalysts have high surface areas (greater than 140 m²/g) and high compacted bulk densities (0.65—0.95 g/cm³, more narrowly 0.7—0.95 g/cm³). The high surface area increases reaction rates due to generally increased dispersion of the active components. Higher

density catalysts allow one to load a larger amount of active metals and promoter per reactor volume, a factor which is commercially important. The metal and phosphorus content specified above provides the high activity per reactor volume. Lower metal contents result in catalysts exerting too low activities for proper use in the process according to the present invention. Higher metal contents do not contribute significantly to the performance and thus lead to an insufficient use of the metals and higher cost for the catalyst. Since deposits of coke are thought to cause the majority of the catalyst deactivation, fresh catalyst pore volume should be at a modest level (0.4—0.8 cm³/g, more narrowly 0.4—0.6 cm³/g).

A low-phosphorus or no-phosphorus conventional hydrotreating catalyst is used in the second zone of the catalyst system. Co and/or Ni containing conventional catalysts can be suitably applied. The second zone catalyst differs from the first zone catalyst primarily in its low-phosphorus content (less than 0.5%w). The preferred catalyst contains less than about 0.5%w phosphorus and comprises a component from group VIB and a group VIII metal or metal oxide, or metal sulphide and/or mixtures thereof composited with a support. Preferably, the catalyst comprises a nickel and/or cobalt component and a molybdenum and/or tungsten component with an alumina support which may additionally contain silica. Preferred metal contents are up to 10%w, usually 1 to 5%w of group VIII metal component(s) calculated on the base of the metal content, and from 3 to 30%w of group VIB metal component(s) in the base of the metal content. A more preferred catalyst comprises a cobalt or nickel component and a molybdenum component with an alumina support.

The present invention preferably relates to a process for hydrotreating oils having a tendency to deactivate hydrotreating catalysts by coke formation, by passing a) oils having a final boiling point above 538°C and having less than 2%w of heptane asphaltenes, b) oils having a final boiling point from 343°C to 538°C, or c) mixtures thereof downwardly with hydrogen or a hydrogen-containing gas (mixture) into a hydrotreating zone over a stacked-bed of two hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to H₂S, wherein said stacked-bed comprises an upper zone containing of from 15—85%v, based on total catalyst, of a high-activity hydrotreating catalyst which comprises from 2—4%w nickel, from 8—15%w molybdenum and from 1—4%w phosphorus supported on a carrier consisting mostly of alumina, and a lower zone containing of from 15—85%v, basis total catalyst, of a high-activity, hydrodesulphurization catalyst which comprises from 2—4%w cobalt and/or nickel, from 8—15%w molybdenum and less than 0.5%w phosphorus supported on a carrier consisting mostly of alumina; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid oil having reduced sulphur and/or heavy metal content.

The physical characterizations of the catalysts referred to herein are common to those skilled in the catalyst development art. Surface areas refer to nitrogen adsorption surface areas preferably determined by at least three points. Pore size distributions are determined by mercury intrusion and calculated with a 130 degree contact angle. Pore volumes stated are water pore volumes and indicate the volume of water per weight of catalyst necessary to fill the catalyst pores to an incipient wetness of the catalyst.

The volume of the first catalyst zone in the present invention is from 15 to 85%v of the main catalyst charge. The remaining fraction of the main catalyst charge is composed of the second catalyst. The division of the catalyst volumes over the zones in the bed depends upon the requirement for nitrogen conversion versus the requirements for stability and other hydrotreating reactions such as sulphur and metals removal. Stacked-beds can be used to tailor the amount of nitrogen removal, sulphur and metals removal, and system stability. An increase in the first catalyst will increase the nitrogen removal but will effect the hydrodesulphurization (HDS) activity and stability of the system. Below a catalyst ratio of 15:85 or above a catalyst ratio of 85:15 (upper:lower) the benefits for the stacked-bed system are not large enough to be of practical significance. There is no physical limit on using a smaller percentage of one or the other beds.

The catalyst zones referred to herein may be in the same or different reactors. For existing units with one reactor the catalysts are layered one on top of the other. Many hydrotreating reactors consist of two or more reactors in series. The catalyst zones are not restricted to the particular volume of one vessel and can extend into the next (prior) vessel. The zones discussed herein refer to the main catalyst bed. Small layers of catalysts which are different sizes are frequently used in reactor loading as is known to those skilled in the art. Intervessel heat exchange and/or hydrogen addition may also be used in the process according to the present invention.

The pore size of the catalyst does not play a critical role in the process according to the present invention. The catalysts in the two zones may be based upon the same carrier. Normally, the finished catalysts will have small differences in their average pore sizes due to the differences in the respective metal and phosphorus loadings.

Suitable conditions for operating the catalyst system in accordance with the present invention are given in Table I.

TABLE I

Conditions	Broadest range	Broad range	Narrow range	Narrowest range
Hydrogen partial pressure, bar	6.8—75	20—75	20—55	34—55
Total pressure, bar	13.6—95	27—95	27—75	47—75
Hydrogen/feed ratio, Ni/kg feed	17—1780	17—890	51—255	85—255
Temperature, °C	150—455	285—455	285—425	345—425
Liquid hourly space velocity, kg/kg · h	0.1—10.0	—	0.5—5.0	—

At temperatures below 285°C (for very heavy feeds) and below 150°C (for heavy feeds), the catalysts do not exhibit sufficient activity for the rates of conversion to be of practical significance. At temperatures above 455°C the rate of coking and cracking become excessive resulting in increasingly impractical operations. Reactor metallurgy may also be a limiting constraint above 455°C at the higher pressures.

At liquid space velocities below 0.1 kg/kg · h, the residence time of the oil is long enough to lead to thermal degradation and coking. At liquid space velocities above 10 kg/kg · h the conversion across the reactor is too small to be of practical use. For space velocity and gas-to-oil ratio calculations referred to herein, volumes are measured at 15.5°C and atmospheric pressure.

Hydrogen partial pressure is very important in determining the rate of catalyst coking and deactivation. At pressures below 6.8 bar, the catalyst system cokes too rapidly even with better quality oil containing high boiling components. At pressures above 75 bar, the deactivation mechanism of the catalyst system appears to be predominantly that of metals deposition, if present, which results in pore-mouth plugging. Catalysts of varying porosity can be used to address deactivation by metals deposition, as is known by those skilled in the art. The hydrogen to feed ratio to be applied in the process according to the present invention is required to be above 17 Ni/kg feed since the reactions occurring during hydrotreating consume hydrogen, resulting in a deficiency of hydrogen at the bottom of the reactor. This deficiency may cause rapid coking of the catalyst and leads to impractical operation. At hydrogen to feed ratios in excess of 890 Ni/kg feed, no substantial benefit is obtained; thus the expense of compression beyond this rate is not warranted.

Nitrogen removal is an important factor in hydrotreating heavy oils. Catalysts without phosphorus can be more stable with heavy oils under the conditions noted above; however, nitrogen removal activity is low for no-phosphorus catalysts relative to their phosphorus promoted counterparts. Additionally, Co promoted catalysts are less active for nitrogen removal than are Ni promoted catalysts. Stacked catalyst beds can be used to tailor the amount of nitrogen removal, sulphur and metals removal, and system stability. It has been found that a stacked-bed system also improves activities (other than nitrogen removal) as well as the stability of the overall catalyst system relative to either catalyst used individually. The stacked-bed catalyst system is applicable when processing feeds under conditions where a heavy feed is causing deactivation primarily by coking.

The process according to the present invention should be operated at conditions suitable to remove at least 25% and generally conditions will be applied to remove 30—80%, more preferably 45—75%, of the sulphur in the feed. When metals such as Ni and V are present in the feed and demetallization is the primary focus the process can be operated at the lower levels of desulphurization. When there is little metal in the feed and demetallization is not the primary goal, one can operate the process at higher sulphur removal rates.

The invention is accompanied by Figures 1 and 2 wherein some of the results as described in the Examples are depicted graphically.

Figure 1 represents a graph showing the advantage obtained in the reactor inlet temperature as a function of time when the stacked-bed according to the present invention is utilized.

Figure 2 represents a graph showing the advantage obtained in the reactor outlet temperature as a function of time when the stacked-bed according to the present invention is utilized.

The following Examples are presented to illustrate the present invention.

Example 1

A catalyst A containing nickel, molybdenum and phosphorus supported on a gamma alumina carrier was prepared from commercially available alumina powders. This carrier was extruded into 1.6 mm pellets

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having a trilobal cross section. The pellets were dried and calcined before being impregnated with the appropriate catalytically active metals by a dry pore volume method i.e., by adding only enough solution to fill the alumina pore volume. Carriers containing in addition to alumina, a few per cent of other components like silica or magnesia can also be applied. An appropriate aqueous solution of nickel nitrate, nickel carbonate, phosphoric acid, hydrogen peroxide, and ammonium molybdate was used to impregnate the carrier. The metal loadings and some properties of the dried, calcined catalyst (A) are given in Table II.

A catalyst B containing cobalt and molybdenum supported on a similar alumina carrier as used to prepare catalyst A was prepared. Likewise, this carrier was also extruded into 1.6 mm pellets having a trilobal cross-section. The pellets were dried before being impregnated with the appropriate catalytically active metals by a dry pore volume method. An appropriate aqueous solution of cobalt carbonate, ammonium dimolybdate and ammonia was used to impregnate the carrier. The metal loadings and properties of the dried, calcined catalyst (B) are also given in Table II.

TABLE II

Catalyst	A	B
Diameter	1.6 mm	1.6 mm
Cross-section	Trilobal	Trilobal
Composition, %w		
Ni	3.0	—
Co	—	3.2
Mo	13.0	9.6
P	3.2	—
Compacted bulk density, g/cm ³	0.82	0.71
Surface Area, m ² /g	164	226
Hg-pore volume, cm ³ /g	0.47	0.61

Three different commercial runs with a main catalyst charge of a Ni-Mo-P/alumina catalyst, a Co-Mo/alumina catalyst and a stacked-bed of a Ni-Mo-P/alumina catalyst over a Co-Mo/alumina catalyst were carried out. In Fig. 1 the reactor inlet temperature (RIT in °C) necessary to maintain 0.3% weight sulphur in the product is graphically represented as a function of time (days), which is a convenient measure of general catalyst activity. The Ni-Mo-P catalyst data are represented as circles (upper line), the Co-Mo catalyst data as triangles (middle line) and the stacked catalyst data as diamonds (lower line). The stacked-bed system has good activity and stability for sulphur removal as well as denitrification advantages. The average feed properties and average unit conditions are given in Table III. The feed applied was a heavy vacuum gas oil having a final boiling point above 538°C and containing less than 2%w of heptane asphaltenes. Feed to the unit and unit conditions were remarkably constant during the runs considering the unit is a commercial unit. In the stacked-bed system the Ni-Mo-P catalyst formed about 33% of the main catalyst load while the Co-Mo catalyst made up the remainder of the main catalyst load. Oil and gas flowed in a single-stage and serially over first the Ni-Mo-P catalyst and then over the Co-Mo catalyst.

The main advantages of the stacked-bed system shown by this Example comprises a) a significant increase in catalyst stability as can be seen in Fig. 1 where the increase in RIT with time is significantly less for the stacked-bed system (3.1°C/month versus 12.5°C/month) relative to the single catalyst system; b) an increase in catalyst activity as represented by about a 8.1°C lower initial RIT for the same level of sulphur in the product; c) a resulting greatly improved estimated catalyst life of about 400% for the stacked-bed relative to the single bed due to the improvements in activity and stability. An end of run temperature of 416°C and a continued linear decline rate was used to estimate the catalyst life of the stacked-bed system.

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TABLE III
Feed/process properties
Hydrogen partial pressure 38 bar

5	Liquid hourly space velocity	3 kg/kg · h
	Sulphur, % wt	1.1
	Nickel, ppm	0.6
10	Vanadium, ppm	0.7
	RCR, %wt	0.3
	TBP-GLC, °C	
	IBP/10%	265/347
15	90/95%	524/538

Example 2

A second set of two commercial runs with a Ni-Mo-P/alumina catalyst and a stacked-bed of a Ni-Mo-P/alumina catalyst over a Co-Mo/alumina catalyst was also carried out. A Ni-Mo-P/alumina catalyst would be one that one skilled in the art would traditionally have chosen for this feedstock when considering hydrogenation, denitrification, and desulphurization catalyst activity rather than a Co-Mo catalyst. Table IV summarizes approximate average unit conditions and feedstock. The oil is a blend of straight run vacuum gas oil (distilled from non-cracked oil) and a coker heavy gas oil. In Table V the approximate average performance for the two runs at two catalyst ages is summarized and in Figure 2 the reactor outlet temperature necessary to maintain 0.75% weight and 0.60% weight sulphur in the product for the single catalyst and the stacked bed system is depicted as a function of time (days).

The main advantage of the stacked-bed system relative to the single bed system shown by this Example comprise a) higher sulphur conversion, even at lower operating temperatures, b) greater catalyst stability when processing the same type feed—about first 60 days—, c) processing a heavier feed at comparable stabilities—about after 60 days—, and d) greater hydrogen addition even at lower operating temperatures. It can be seen from Fig. 2 that the single bed system has a lower start of run temperature in the first one or two weeks but this temperature relates to 0.75%w sulphur in the product where the temperature for the stacked-bed system relates to 0.60%w sulphur in the product. To obtain also 0.6% weight sulphur in the product initially with the single bed system an additional 7.5°C would be required, thereby making the single bed about 4.4°C less active initially. It will be clear from Fig. 2 that although the two different catalyst configurations have similar temperatures at the start of run (for the different sulphur targets), the stacked-bed system has about a 12.5°C advantage after 2 months indicating the greater stability when processing the same type feed containing about 30% by volume of the coker material. After about 60 days the coking tendency of the feed to the single bed system was reduced by decreasing the amount of the full range coker heavy gas oil from about 30% down to 20% by volume (indicated by an arrow in the upper line of Fig. 2). The single bed system stability improved with the feed having reduced coking tendency and is beginning to approach that of the stacked-bed system although still at the higher sulphur in product level. This data shows that the stacked-bed system can be used to process a feed with greater coking tendency with equivalent catalysts life and for this case even with higher sulphur conversion. Table V provides some data indicating that the hydrogen consumption of the stacked-bed system is some 6% better (lower) than that of the single bed system. The best comparison is at the 1 month point where the catalysts are processing the same feed. The larger hydrogen consumption is reflected in the greater temperature rise across the reactor (Reactor delta T in Table V); hydrogen addition is a major factor in the heat release during hydrotreating.

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TABLE IV
Feed properties and operating parameters

5	Feed	Vacuum gas oil/ coker heavy gas oil	
	Ratio	40/60	
	End Point, °C	above 538°C	
	Feed Sulphur, %w	~3	
10	LHSV, kg/kg · h	2.76	
	H ₂ pressure (Reactor inlet) bar	49.3	
	H ₂ /oil ratio (NI/kg feed)	289	
15	Individual feedstocks	Vac. gas oil	Coker heavy gas oil
	Molecular weight	369	312
	Carbon, %w	85.4	85.2
20	Hydrogen, %w	11.8	11.0
	Sulphur, %w	2.5	3.2
25	TBP-GLC wt 538°C	91.2	95.0

TABLE V
Catalysts and performance

30	Catalyst age	1 month		4 months	
35	Catalyst*	1	1 & 2	1	1 & 2
	Reactor temp., out, °C	360	357.2	376.7	362.8
	Reactor delta T, °C	37.5	40.6	34.4	40.6
40	H ₂ consumption, NI/kg feed	63.8	68	63.8	68
	Product sulphur, %w	0.75	0.6	0.75	0.6
45	*Catalyst 1 is Ni-Mo-P Catalyst 2 is Co-Mo				

Example 3

50 A third set of two commercial runs with a Ni-Mo-P/alumina catalyst and a stacked-bed of a Ni-Mo-P/alumina catalyst and a Co-Mo/alumina catalyst was also made. The feed used has a final boiling point between 343°C and 538°C and contained straight run light gas oil, coker naphtha, coker light gas oil and light cycle oil. In Table VI the approximate average unit conditions and feed stock properties are summarized. Analysis of the data for these two runs showed that the stacked-bed used in accordance with the present instant invention showed the following advantages when compared to the single catalyst:

55 a) lower inlet temperature,
b) lower sulphur in the product, and
c) the ability to operate at the same reactor delta temperature even though the reactor inlet temperature was lower.

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TABLE VI
Feed properties and operating parameter

5	Feed gravity	0.92
	Distillation, °C, end point	455
	Feed sulphur, %w	1.3
10	Liquid hourly space velocity kg/kg · h	2.6
	H ₂ pressure (reactor inlet, bar)	35.4
	H ₂ /oil ratio, NI/kg feed	168.3

Claims

1. A process for catalytically hydrotreating hydrocarbon oils at elevated temperature and pressure in the presence of hydrogen in a hydrotreating zone over a stacked-bed of hydrotreating catalysts, characterized in that,
 - a) oils having a final boiling point greater than 538°C and containing less than 2%w of heptane asphaltenes,
 - b) oils having a final boiling point from 343°C to 538°C, or
 - c) mixtures thereof,
 are passed downwardly with hydrogen or a hydrogen-containing gas under conditions suitable to convert more than 25% of the sulphur compounds present to hydrogen sulphide, wherein said stacked-bed comprises an upper zone containing 15—85%v, based on total catalyst, of a hydrotreating catalyst comprising a component from Group VIB of the Periodic Table, a Group VIII metal or metal oxide or metal sulphide and a phosphorus oxide and/or sulphide, and a lower zone containing 15—85%v, based on total catalyst, of a hydrotreating catalyst comprising a component from Group VIB, a Group VIII metal or metal oxide or metal sulphide and less than 0.5%w of phosphorus; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having a reduced heteroatom content.
2. A process according to claim 1, wherein a stacked-bed is used containing an upper zone containing up to 10%w of a Group VIII component, 3—15%w of a Group VIB component and 0.1—10%w of phosphorus, and a lower zone containing up to 10%w of a Group VIII component and 3—30%w of a Group VIB component.
3. A process according to claim 1 or 2, wherein a stacked-bed is used containing an upper zone comprising a nickel component, a molybdenum and/or tungsten component and phosphorus on an alumina support which may additionally contain silica, and a lower zone comprising a nickel and/or cobalt component and a molybdenum and/or tungsten component on an alumina support which may additionally contain silica.
4. A process according to claim 3, wherein a stacked-bed is used containing an upper zone containing 2—4%w of nickel, 8—15%w of molybdenum and 1—4%w of phosphorus supported on a carrier consisting mostly of alumina, and a lower zone containing 2—4%w of cobalt and/or nickel, from 8—15%w of molybdenum and less than 0.5%w of phosphorus supported on a carrier consisting mostly of alumina.
5. A process according to any of claims 1—4, wherein a stacked-bed is used wherein the upper zone catalyst has a compacted bulk density of 0.65—0.95 g/cm³, in particular 0.76—0.88 g/cm³ and a surface area greater than 140 m²/g, in particular greater than 150 m²/g, and wherein the lower zone catalyst has a compacted bulk density of 0.6—0.8 g/cm³, in particular 0.67—0.69 g/cm³ and a surface area greater than 180 m²/g, in particular greater than 200 m²/g.
6. A process according to any one of claims 1—5, wherein the process is carried out at a hydrogen pressure not exceeding 75 bar.
7. A process according to any one of claims 1—6, wherein use is made of a stacked-bed catalyst containing in its lower zone 2—4%w of cobalt and essentially no nickel and no phosphorus.
8. A process according to any one of claims 1—6, wherein use is made of a stacked-bed catalyst containing in its lower zone 2—4%w of nickel and essentially no cobalt and no phosphorus.
9. A process according to any one of claims 1—8, wherein use is made of a stacked-bed containing a trilobally shaped catalyst in the upper and/or the lower zone.
10. A process according to claim 9, wherein use is made of a catalyst carrier extruded into a trilobal shape before impregnation.
11. A process according to any one of claims 1—10, wherein the hydrotreating zone is contained in a single reactor and the upper zone of the stacked-bed catalyst comprises about one-third of the total catalyst volume.
12. A process according to any one of claims 1—11, wherein hydrocarbon oils having a tendency to deactivate hydrotreating catalysts by coke formation are hydrotreated by passing:
 - a) oils having a final boiling point above 538°C and having less than 2%w of heptane asphaltenes,

- b) oils having a final boiling point from 343°C to 538°C, or
 c) mixtures thereof,
 downwardly with hydrogen or a hydrogen-containing gas into a hydrotreating zone over a stacked-bed of two hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to H₂S; said stacked-bed comprising an upper zone containing of from 15—85%v, based on total catalyst, of a high-activity hydrotreating catalyst which comprises from 2—4%w nickel, from 8—15%w molybdenum and from 1—4%w phosphorus supported on a carrier consisting mostly of alumina, said catalyst having a compacted bulk density of 0.65—0.95 g/cm³ and a surface area greater than 140 m²/g; and a lower zone containing from 15—85%v, based on total catalyst, of a high-activity, hydrodesulphurization catalyst which comprises from 2—4%w cobalt and/or nickel and from 8—15%w molybdenum and less than 0.5%w phosphorus supported on a carrier consisting mostly of alumina, said catalyst having a compacted bulk density of 0.6—0.8 g/cm³ and a surface area greater than 180 m²/g; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having reduced sulphur and/or heavy metal content.

Patentansprüche

1. Ein Verfahren zur katalytischen Hydrobehandlung von Kohlenwasserstoffölen bei erhöhter Temperatur und erhöhtem Druck in Gegenwart von Wasserstoff in einer Hydrobehandlungszone über einem Schichtbett aus hydrobehandelnden Katalysatoren, dadurch gekennzeichnet, daß
 - a) Öle mit einem Endsiedepunkt von mehr als 538°C und mit einem Gehalt von weniger als 2 Gewichtsprozent Heptanasphaltenen,
 - b) Öle mit einem Endsiedepunkt von 343°C bis 538°C oder
 - c) Mischungen davon,
 zusammen mit Wasserstoff oder einem Wasserstoff enthaltenden Gas unter für die Umwandlung von mehr als 25% der vorhandenen Schwefelverbindungen in Schwefelwasserstoff geeigneten Bedingungen abwärts geleitet werden, wobei das genannte Schichtbett eine obere Zone, enthaltend 15 bis 85 Volumenprozent, bezogen auf den Gesamtkatalysator, eines hydrobehandelnden Katalysators, umfassend eine Komponente aus der Gruppe VIB des Periodischen Systems der Elemente, ein Metall, Metalloxid oder Metallsulfid der Gruppe VIII und ein Phosphoroxid und/oder -sulfid, und eine untere Zone enthaltend 15 bis 85 Volumenprozent, bezogen auf den Gesamtkatalysator, eines hydrobehandelnden Katalysators umfassend eine Komponente der Gruppe VIB, ein Metall, Metalloxid oder Metallsulfid der Gruppe VIII und weniger als 0,5 Gewichtsprozent Phosphor, umfaßt; und das Reaktionsprodukt aus der genannten Hydrobehandlungszone in ein wasserstoffreiches Gas und ein flüssiges Kohlenwasserstofföl mit reduziertem Heteroatomgehalt aufgetrennt wird.
2. Ein Verfahren nach Anspruch 1, in welchem ein Schichtbett, umfassend eine obere Zone, enthaltend bis zu 10 Gewichtsprozent einer Komponente der Gruppe VIII, 3 bis 15 Gewichtsprozent einer Komponente der Gruppe VIB und 0,1 bis 10 Gewichtsprozent Phosphor, und eine untere Zone, enthaltend bis zu 10 Gewichtsprozent einer Komponente der Gruppe VIII und 3 bis 30 Gewichtsprozent einer Komponente der Gruppe VIB, verwendet wird.
3. Ein Verfahren nach Anspruch 1 oder 2, in welchem ein Schichtbett, umfassend eine obere Zone, enthaltend eine Nickelkomponente, eine Molybdän- und/oder Wolframkomponente und Phosphor auf einem Aluminiumoxidträger, welcher zusätzlich Siliciumdioxid enthalten kann, und eine untere Zone, enthaltend eine Nickel- und/oder Kobaltkomponente und eine Molybdän- und oder Wolframkomponente auf einem Aluminiumoxidträger, welcher zusätzlich Siliciumdioxid enthalten kann, verwendet wird.
4. Ein Verfahren nach Anspruch 3, in welchem ein Schichtbett umfassend eine obere Zone, enthaltend 2 bis 4 Gewichtsprozent Nickel, 8 bis 15 Gewichtsprozent Molybdän und 1 bis 4 Gewichtsprozent Phosphor auf einem Träger, welcher im wesentlichen aus Aluminiumoxid besteht, und eine untere Zone, enthaltend 2 bis 4 Gewichtsprozent Kobalt und/oder Nickel, 8 bis 15 Gewichtsprozent Molybdän und weniger als 0,5 Gewichtsprozent Phosphor auf einem Träger, der im wesentlichen aus Aluminiumoxid besteht, verwendet wird.
5. Ein Verfahren nach einem der Ansprüche 1 bis 4, in welchem ein Schichtbett verwendet wird, bei welchem der Katalysator der oberen Zone eine verdichtete Schüttdichte von 0,65 bis 0,95 g/cm³, vorzugsweise von 0,76 bis 0,88 g/cm³ und eine Oberflächenausdehnung von mehr als 140 m²/g, vorzugsweise von mehr als 150 m²/g, aufweist, und der Katalysator der unteren Zone eine verdichtete Schüttdichte von 0,6 bis 0,8 g/cm³, vorzugsweise von 0,67—0,69 g/cm³ und eine Oberflächenausdehnung von mehr als 180 m²/g, vorzugsweise von mehr als 200 m²/g, aufweist.
6. Ein Verfahren nach einem der Ansprüche 1 bis 5, in welchem das Verfahren bei einem Wasserstoffdruck von nicht mehr als 75 bar durchgeführt wird.
7. Ein Verfahren nach einem der Ansprüche 1 bis 6, in welchem ein Schichtbettkatalysator verwendet wird, welcher in seiner unteren Zone 2 bis 4 Gewichtsprozent Kobalt und im wesentlichen kein Nickel und keinen Phosphor enthält.
8. Ein Verfahren nach einem der Ansprüche 1 bis 6, in welchem ein Schichtbettkatalysators eingesetzt wird, der in seiner unteren Zone 2 bis 4 Gewichtsprozent Nickel und im wesentlichen kein Kobalt und keinen Phosphor enthält.

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9. Ein Verfahren nach einem der Ansprüche 1 bis 8, in welchem ein Schichtbett verwendet wird, das einen dreilappig geformten Katalysator in der oberen und/oder unteren Zone enthält.
10. Ein Verfahren nach Anspruch 9, in welchem ein Katalysatorträger eingesetzt wird, der vor dem Imprägnieren in dreilappiger Form extrudiert worden ist.
11. Ein Verfahren nach einem der Ansprüche 1 bis 10, in welchem die Hydrobehandlungszone in einem einzigen Reaktor enthalten ist und die obere Zone des Schichtbettes ca. 1/3 des gesamten Katalysatorvolumens ausmacht.
12. Ein Verfahren nach einem der Ansprüche 1 bis 11, in welchem Kohlenwasserstofföle mit einer Neigung, hydrobehandelnde Katalysatoren unter Bildung von Koks zu deaktivieren durch die folgenden Schritte hydrobehandelt werden:
- a) Öle mit einem Endsiedepunkt von 538°C und einem Gehalt von weniger als 2 Gewichtsprozent Heptanasphaltenen,
 - b) Öle mit einem Endsiedepunkt von 343°C bis 538°C, oder
 - c) Mischungen davon
- werden mit Wasserstoff und wasserstoffhaltigem Gas in einer Hydrobehandlungszone über ein Schichtbett aus zwei hydrobehandelnden Katalysatoren bei für die Umwandlung von mehr als 25% der vorhandenen Schwefelverbindungen in H₂S geeigneten Bedingungen nach unten geleitet; das genannte Schichtbett enthält eine obere Zone, enthaltend von 15 bis 85 Volumprozent, bezogen auf den Gesamtkatalysator, eines hochaktiven hydrobehandelnden Katalysators, welcher 2 bis 4 Gewichtsprozent Nickel, 8 bis 15 Gewichtsprozent Molybdän und 1 bis 4 Gewichtsprozent Phosphor auf einem Träger, der im wesentlichen aus Aluminiumoxid besteht, enthält, wobei dieser Katalysator eine verdichtete Schüttdichte von 0,65 bis 0,95 g/cm³ und eine Oberflächenausdehnung von mehr als 140 m²/g aufweist; und eine untere Zone, enthaltend 15 bis 85 Volumenprozent, bezogen auf den Gesamtkatalysator, eines hochaktiven Hydroentschwefelungskatalysators, welcher 2 bis 4 Gewichtsprozent Kobalt und/oder Nickel und 8 bis 15 Gewichtsprozent Molybdän und weniger als 0,5 Gewichtsprozent Phosphor auf einem Träger, der zum größten Teil aus Aluminiumoxid besteht, enthält, wobei dieser Katalysator eine verdichtete Schüttdichte von 0,6 bis 0,8 g/cm³ und eine Oberflächenausdehnung von mehr als 180 m²/g aufweist; und dann wird das Reaktionsprodukt aus der genannten Hydrobehandlungszone in ein wasserstoffreiches Gas und ein flüssiges Kohlenwasserstofföl mit reduziertem Schwefel- und/oder Schwermetallgehalt aufgetrennt.

Revendications

1. Un procédé pour l'hydrotraitement catalytique d'huiles d'hydrocarbures à température et pression élevées en présence d'hydrogène dans une zone d'hydrotraitement sur un lit empilé de catalyseurs d'hydrotraitement, caractérisé en ce que
 - a) des huiles ayant un point final d'ébullition au-dessus de 538°C et contenant moins de 2% en poids d'asphaltènes insolubles dans l'heptane,
 - b) des huiles ayant un point final d'ébullition compris entre 343°C et 538°C, ou
 - c) leurs mélangessont passés de haut en bas avec de l'hydrogène ou un gaz contenant de l'hydrogène dans des conditions convenables pour transformer plus de 25% des composés du soufre présente en hydrogène sulfuré, où le lit empilé comprend une zone supérieure contenant 15—85% en volume, par rapport au catalyseur total, d'un catalyseur d'hydrotraitement comprenant un constituant du groupe VIB du tableau périodique des éléments, un métal ou oxyde de métal ou sulfure de métal du groupe VIII et un oxyde et/ou un sulfure de phosphore, et une zone inférieure contenant 15—85% en volume, par rapport au catalyseur total, d'un catalyseur d'hydrotraitement comprenant un constituant du groupe VIB, un métal ou oxyde de métal ou sulfure de métal du groupe VIII et moins de 0,5% en poids de phosphore; et on sépare le produit de réaction sortant de la zone d'hydrotraitement en un gaz riche en hydrogène et une huile d'hydrocarbures liquide ayant une teneur réduite en hétéro-atomes.
2. Un procédé selon la revendication 1, dans lequel on utilise un lit empilé comprenant une zone supérieure contenant jusqu'à 10% en poids d'un constituant du groupe VIII, 3—15% en poids d'un constituant du groupe VIB et 0,1—10% en poids de phosphore, et une zone inférieure contenant jusqu'à 10% en poids d'un constituant du groupe VIII et 3—30% en poids d'un constituant du groupe VIB.
3. Un procédé selon la revendication 1 ou 2, dans lequel on utilise un lit empilé contenant une zone supérieure comprenant un constituant nickel, un constituant molybdène et/ou tungstène et du phosphore sur un support d'alumine qui peut contenir en outre de la silice, et une zone inférieure comprenant un constituant nickel et/ou cobalt et un constituant molybdène et/ou tungstène sur un support d'alumine qui peut contenir en outre de la silice.
4. Un procédé selon la revendication 3, dans lequel on utilise un lit empilé contenant une zone supérieure contenant 2—4% en poids de nickel, 8—15% en poids de molybdène et 1—4% en poids de phosphore déposés sur un support constitué principalement d'alumine, et une zone inférieure contenant 2—4% en poids de cobalt et/ou de nickel, de 8 à 15% en poids de molybdène et moins de 0,5% en poids de phosphore déposés sur un support constitué principalement d'alumine.
5. Un procédé selon l'une quelconque des revendications 1—4, dans lequel on utilise un lit empilé dans lequel le catalyseur de la zone supérieure a une masse volumique apparente à l'état tassé de 0,65—0,95

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g/cm³, en particulier de 0,76—0,88 g/cm³ et une surface spécifique supérieure à 140 m²/g, en particulier supérieure à 150 m²/g, et où le catalyseur de la zone inférieure a une masse volumique apparente à l'état tassé de 0,6—0,8 g/cm³, en particulier de 0,67—0,69 g/cm³ et une surface spécifique supérieure à 180 m²/g, en particulier supérieure à 200 m²/g.

5 6. Un procédé selon l'une quelconque des revendications 1—5, dans lequel le procédé est mis en oeuvre à une pression d'hydrogène ne dépassant pas 75 bars.

7. Un procédé selon l'une quelconque des revendications 1—6, dans lequel on utilise un catalyseur en lit empilé contenant dans sa zone inférieure 2—4% en poids de cobalt et essentiellement pas de nickel ni de phosphore.

10 8. Un procédé selon l'une quelconque des revendications 1—6, dans lequel on utilise un catalyseur en lit empilé contenant dans sa zone inférieure 2—4% en poids de nickel et essentiellement pas de cobalt ni de phosphore.

9. Un procédé selon l'une quelconque des revendications 1—8, dans lequel on utilise un lit empilé contenant un catalyseur de forme trilobée dans la zone supérieure et/ou la zone inférieure.

15 10. Un procédé selon la revendication 9, dans lequel on utilise un support de catalyseur extrudé à une forme trilobée avant imprégnation.

11. Un procédé selon l'une quelconque des revendications 1—10, dans lequel la zone d'hydrotraitement est contenue dans un seul réacteur et la zone supérieure du catalyseur en lit empilé comprend environ un tiers du volume total du catalyseur.

20 12. Un procédé selon l'une quelconque des revendications 1—11, dans lequel des huiles d'hydrocarbures ayant tendance à désactiver les catalyseurs d'hydrotraitement par formation de coke sont hydrotraitées en faisant passer:

a) des huiles ayant un point final d'ébullition au-dessus de 538°C et ayant moins de 2% en poids d'asphaltènes insolubles dans l'heptane,

25 b) des huiles ayant un point final d'ébullition compris entre 343°C et 538°C, ou

c) des mélanges de telles huiles,

de haut en bas avec de l'hydrogène ou un gaz contenant de l'hydrogène dans une zone d'hydrotraitement sur un lit empilé de deux catalyseurs d'hydrotraitement dans des conditions convenables pour transformer plus de 25% des composés du soufre présents en H₂S; ce lit empilé comprenant une zone supérieure 30 contenant de 15 à 85% en volume, par rapport au catalyseur total, d'un catalyseur d'hydrotraitement d'une haute activité qui comprend de 2 à 4% en poids de nickel, de 8 à 15% en poids de molybdène et de 1 à 4% en poids de phosphore déposés sur un support constitué principalement d'alumine, ce catalyseur ayant une masse volumique apparente à l'état tassé de 0,65—0,95 g/cm³ et une surface spécifique supérieure à 140 m²/g; et une zone inférieure contenant de 15 à 85% en volume, par rapport au catalyseur total, d'un 35 catalyseur d'hydrodésulfuration d'une haute activité qui comprend de 2 à 4% en poids de cobalt et/ou de nickel et de 8 à 15% en poids de molybdène et moins de 0,5% en poids de phosphore déposés sur un support constitué principalement d'alumine, ce catalyseur ayant une masse volumique apparente à l'état tassé de 0,6—0,8 g/cm³ et une surface spécifique supérieure à 180 m²/g; et en séparant le produit de réaction sortant de la zone d'hydrotraitement en un gaz riche en hydrogène et une huile d'hydrocarbures

40 liquide ayant une teneur réduite en soufre et/ou en métaux lourds.

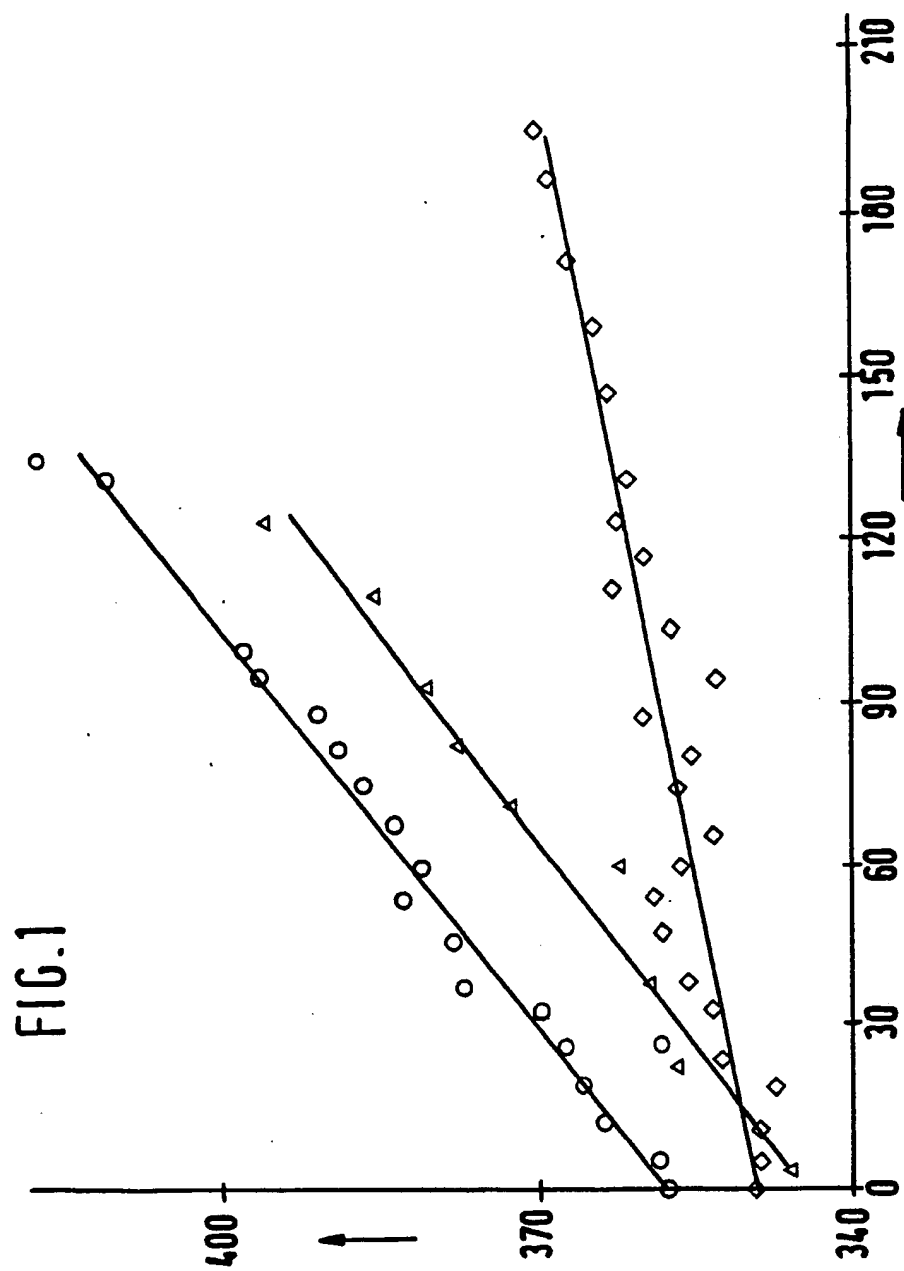
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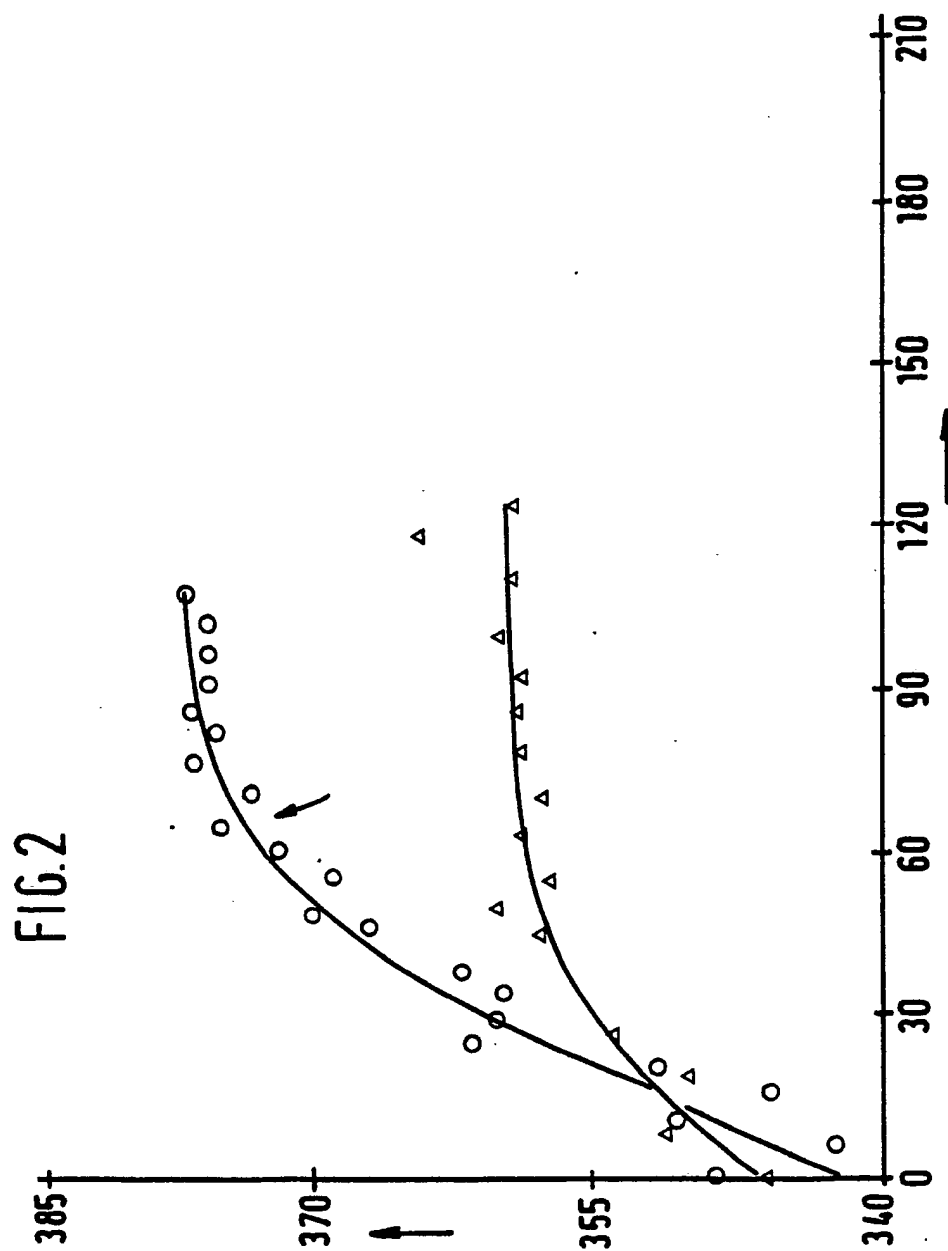
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(54) Single-stage hydrotreating process

Einstufiges Raffinationsverfahren

Procédé d'hydrotraitement en une étape

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(56) References cited:

EP-A- 0 008 424	EP-A- 0 112 667
EP-A- 0 126 250	FR-A- 2 212 417
GB-A- 2 032 796	GB-A- 2 055 602
GB-A- 2 073 770	US-A- 3 287 280
US-A- 4 016 067	US-A- 4 406 779

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Description

The present invention relates to a single-stage hydrotreating process for treating heavy oils using catalysts arranged in a particular manner, referenced to herein as "stacked bed". It particularly relates to a single-stage hydrotreating process for treating oils having a tendency to deactivate hydrotreating catalysts by coke formation, these being oils with high boiling components and/or oils with a low asphaltene content and very high boiling components, with a particular stacked bed catalyst arrangement. It has been found that the use of a stacked bed increases the catalyst life or allows increased conversions relative to the more traditional catalysts used for the treating of these oils. The invention is particularly useful for meeting the demands of increasing hydrotreatment severity, such as sulphur removal, for poorer quality heavy oil fractions both directly distilled or extracted from crude or crude fraction and oil fractions from thermal, steam, or catalytic cracking processes including mixtures of any of these materials.

The continual changes in the refining industry such as the trend to poorer quality crudes and the continual increase in the stringency of oil product specifications (e.g. lower allowed sulphur content) is in part requiring the refiner to increase the severity of hydrotreating of traditional oil fractions and/or process fractions not traditionally treated. The increased severity and/or unusual feed generally have been causing increased deactivation of hydrotreating catalysts. By using the process according to the present invention the run length of a hydrotreating process with these oil fractions can be increased and/or higher severity operation and/or processing poorer quality oils can be allowed.

The use of lower price or locally available crudes frequently results in increased sulphur and/or nitrogen content of the oil fractions. Conversion processes such as thermal cracking, coking and catalytic cracking are either being brought on-stream or are already processing poorer quality oils. The products from such processes are laden with heteroatoms such as sulphur and are more hydrogen deficient relative to products from better quality crudes or oils distilled directly from crude or crude fractions. As a result, the products of the conversion processes and/or poorer crudes have to be additionally hydrotreated to meet specifications or to prepare for further treating/conversion. However, the higher operating temperatures required to remove the additional heteroatoms and adding additional hydrogen in addition to the hydrogen-deficient coke-like nature of these feeds result in increasing deactivation of the hydrotreating catalysts due to coking. Any increase in hydrotreating catalyst activity and/or stability would enable refiners to upgrade the lower value poor quality and/or cracked oils at a significant economic benefit.

It is well known that hydrogen-deficient poor quality oils can be hydrotreated/hydrorefined with low catalyst deactivation rates at higher hydrotreating unit conditions-higher hydrogen pressure, and/or hydrogen-to-oil ratio, and/or oil-catalyst contact time. To stay within the physical or design constraints of a unit or to continue to process the required volumes of oil, only relatively small variations in these parameters can be made. As a result, very expensive hydrotreating equipment must be added to meet the changing goals unless catalysts with longer lives are available. Alternatively, the refiner has to accept very short catalyst lives and increased down time for frequent catalyst changes or use continuous or semicontinuous regeneration facilities. Larger and/or more vessels and additional equipment would be needed to process a given quantity of feedstock with these options. Of particular importance to a refiner is the ability to process the hydrogen-deficient and/or poorer quality oils in existing hydrotreating units which do not have sufficient hydrogen pressure to prevent uneconomically rapid catalyst activity loss with existing catalysts utilized in a non-stacked bed configuration. Thus, improved processes and highly stable catalysts are in great demand.

Several two-stage hydrotreating processes have been proposed in the art to overcome some of the difficulties of hydrotreating heavy oils. Reference is made to five patent specifications, wherein use is made of two catalyst reactor vessels.

In U.S. patent specification 3,766,058 a two-stage process is disclosed for hydrodesulphurizing high-sulphur vacuum residues. In the first stage some of the sulphur is removed and some hydrogenation of the feed occurs, preferably over a cobalt-molybdenum catalyst supported on a composite of ZnO and Al₂O₃. In the second stage the effluent is treated under conditions to provide hydrocracking and desulphurization of asphaltenes and large resin molecules contained in the feed, preferably over molybdenum supported on alumina or silica, wherein the second catalyst has a greater average pore diameter than the first catalyst.

In U.S. patent specification 4,016,069 a two-stage process is disclosed for hydrodesulphurizing metal- and sulphur-containing asphaltenic heavy oils with an interstage flashing step and with partial feed oil bypass around the first stage.

In U.S. patent specification 4,048,060 a two-stage hydrodesulphurization and hydrodemetallization process is disclosed wherein a different catalyst is utilized in each stage and wherein the second stage catalyst has a larger pore size than the first catalyst and a specific pore size distribution.

In U.S. patent specification 4,166,026 a two-step process is taught wherein a heavy hydrocarbon oil containing large amounts of asphaltenes and heavy metals is hydrodemetallized and selectively cracked in the first step over a catalyst which contains one or more catalytic metals supported on a carrier composed mainly of magnesium silicate. The effluent from the first step, with or without separation of hydrogen-rich gas, is contacted with hydrogen in the presence of a catalyst containing one or more catalytic metals supported on a carrier, preferably alumina or silica-alumina, having a particular pore volume and pore size distribution. This two-step method is claimed to be more efficient

than a conventional process wherein a residual oil is directly hydrodesulphurized in a one-step treatment.

In U.S. patent specification 4,392,945 a two-stage hydrorefining process for treating heavy oils containing certain types of organic sulphur compounds is disclosed wherein use is made of a specific sequence of catalysts with interstage removal of H_2S and NH_3 . A nickel-containing conventional hydrorefining catalyst is present in the first stage. A cobalt-containing conventional hydrorefining catalyst is present in the second stage. The first stage is preferably operated under conditions to effect at least 50%w desulphurization, while the second stage is preferably operated under conditions to achieve at least about 90%w desulphurization, relative to sulphur present in the initial oil feed to the first stage. This process is primarily applicable to distillate gas oil feeds boiling below $343^\circ C$ which contains little or no heavy metals.

All of the patent specifications referred to hereinabove relate to two-stage hydrotreating processes for various hydrocarbon oils utilizing certain advantageous catalysts and/or supports. In some of these processes removal of H_2S and NH_3 is required. However, no reference is made in any of the afore-mentioned patent specifications to a process whereby oils with final boiling points from $343^\circ C$ to $538^\circ C$ and/or oil with a low asphaltene content and with components boiling above $538^\circ C$ can be hydrotreated with significantly improved catalyst life relative to a single catalyst system. It has now been found that by using a specific stacked-bed catalyst arrangement containing different catalytically active compositions, oils with high boiling components (about $343^\circ C$ - $538^\circ C$ and/or oils with a low asphaltene content and with very high boiling components (above $538^\circ C$) can be treated in a single stage hydrotreating process with improved catalyst-system life and/or increased hydrotreating conversions for a given feedstock. The process according to the present invention allows easy conversion of existing catalytic hydrotreating reactors to a stacked bed of specified catalysts. The present process operates well at hydrogen pressures below 75 bar (7500 kPa), so that no additional high pressure reactors need be constructed. The particular stacked bed combination of catalysts in accordance with the invention results in longer runs between replacements or regenerations for a given oil than would be experienced with either catalyst used alone. Alternatively, poorer quality oils can be processed at equivalent conversions or higher conversions for a given oil can be maintained with the same time between replacement or regeneration with the use of the single-stage stacked bed catalyst system according to the present invention. The invention can be applied most usefully in situations where rapid catalyst deactivation is occurring.

The present invention thus relates to a process for catalytically hydrotreating hydrocarbon oils at elevated temperature and pressure in the presence of hydrogen in a hydrotreating zone over a stacked bed of hydrotreating catalysts, characterised in that :

- a) oils having a final boiling point greater than $538^\circ C$ and containing less than 2%w of heptane asphaltenes,
- b) oils having a final boiling point from $343^\circ C$ to $538^\circ C$, or
- c) mixtures thereof, are passed

downwardly with hydrogen or a hydrogen-containing gas into a hydrotreating zone over a stacked-bed of hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to hydrogen sulphide at a hydrogen partial pressure of between 6-8 and 75 bar, wherein said stacked-bed comprises an upper zone containing 15-85%v, based on total catalyst, of a hydrotreating catalyst comprising a component from Group VIB of the Periodic Table, a Group VIII metal or metal oxide or metal sulphide and a phosphorus oxide and/or sulphid in an amount of 1 to 10%w calculated basis phosphorus content and a lower zone containing 15-85%v, based on total catalyst, of a hydrotreating catalyst comprising a component from Group VIB, a Group VIII metal or metal oxide or metal sulphide and less than 0.5%w of phosphorus supported on a carrier consisting essentially of alumina; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having a reduced heteroatom content.

It should be noted that from U.S. patent specification 4,016,067 a process is known for catalytic demetallization and desulphurization using a reactor containing two beds of phosphorus-free catalysts, which each fulfil specific requirements as to surface area and pore size and which both comprise Group VIB and Group VIII-compounds.

The process according to the present invention is particularly suitable for systems where catalyst deactivation due to coking is a constraint. The bottom bed catalyst is preferably Ni-promoted when nitrogen removal is the predominant concern and is preferably Co-promoted when sulphur removal is the predominant concern.

According to the present invention oils having a) final boiling point above $538^\circ C$ whilst having a heptane asphaltenes content less than about 2% by weight, b) final boiling points in the range between $343^\circ C$ and $538^\circ C$, or c) mixtures thereof are contacted with hydrogen or a hydrogen-containing gas and passed downwardly under hydrodesulphurization conditions over a stacked-bed catalyst. The boiling points referred to in the present description are as defined by the American Society for Testing and Materials (ASTM) method D 2887-83 ("Boiling Range Distribution of Petroleum Fractions by Gas Chromatography") and is commonly known as TBP-GLC (true boiling point by gas liquid chromatography). Normal heptane asphaltenes (asphaltenes) as discussed herein are measured by the Institute of Petroleum, London, method IP 143/78 ("Asphaltenes Precipitation with Normal Heptane").

The oils to be used as feedstock in the process according to the present invention will be oils having a tendency

to deactivate hydrotreating catalysts by coke formation, under hydrotreating conditions and particularly under hydrodesulphurization conditions.

Downwardly has been used in this specification to indicate a direction and not an orientation and hence should not be construed to imply an orientation limitation on the instant invention. A downwardly series flow of oil and gas through a reactor is the usual pattern; however, one could invert the reactor conceptually and put oil and gas in at the bottom in which the first catalyst zone (Ni- and P-containing catalyst) should be the first main catalyst contacted by the oil and gas and would thus be in the bottom of the first reactor. As is well known in the industry, multiple reactors connected in series are placed individually. Oil and gas out of one reactor is piped up to the top of the next reactor; however, this process could be inverted. The above-described reactor configurations, as well as others apparent to those skilled in the art, are deemed to be within the scope of this invention.

The feedstocks to be applied in the process in accordance with this invention may be taken from straight run oils (non-cracked) or thermally-, steam-, or catalytically cracked hydrocarbonaceous materials. Suitable feeds include petroleum derived gas oils distilled from crude or crude fractions at atmospheric or at reduced pressure; solvent extracted oils such as extracted oils commonly referred to as Deasphalted Oils; thermally or steamed cracked oils or fractions thereof such as coker gas oils; gas oils or cycle oils from catalytic cracking and mixtures of two or more of the above materials.

Multiple uses of these feedstocks after initial treating in accordance with the process according to the present invention are also possible. Depending on particular feedstocks treated, suitable uses may include feed and additions to feed to units for significant molecular weight reduction such as catalytic cracking units or hydrocracking units; direct use or by blending with other oils or additives for sale as transportation fuels such as diesel oils; or for refinery fuel.

The stacked-bed catalyst system to be used in the process according to the present invention comprises firstly a normally Ni- and P-containing conventional hydrotreating catalyst. The second catalyst to be contacted by the oil normally comprises a low- or no-phosphorus content conventional catalyst. Preferably, the second catalyst contains no phosphorus. The second catalyst is also a conventional catalyst and contains Ni and/or Co in the formulation. When desulphurization is the primary objective of the hydrotreating process, the second catalyst contains Co in preference to Ni; when denitrogenation is the primary objective, the second catalyst preferably contains Ni in preference to Co. The catalysts herein can be prepared by techniques well known in the art. The advantages of this invention primarily accrue from the particular combination of operable hydrotreating catalysts in a stacked-bed rather than from any particular method or manner of fabricating the catalyst.

The first main hydrotreating zone catalyst used in the process according to the present invention suitably comprises a Ni- and P-containing conventional hydrotreating catalyst. Conventional hydrotreating catalysts which are suitable for the first catalyst zone generally comprise a phosphorus oxide and/or sulphide component and a component, selected from group VIB of the Periodic Table and a group VIII metal or metal oxide, or metal sulphide and/or mixtures thereof composited with a support. These catalysts will contain up to 10%w, usually 1 to about 5%w of the group VIII metal compound calculated on the base of the metal content, from 3 to about 15%w of the group VIB metal compound calculated on the base of the metal content, and from 1 to 10%w phosphorus compounds calculated on the base of phosphorus content. Preferably, the catalyst comprises a nickel component and a molybdenum and/or tungsten component with an alumina support which may additionally contain silica. A more preferred catalyst comprises a nickel component, a molybdenum component, and a phosphorus component with an alumina support which may also contain small amounts of silica. Preferred amounts of components range from 2 to 4%w of a nickel component calculated on the base of metal content 8-15%w of a molybdenum component calculated on the base of metal content, and 1 to 4%w, more preferably 2 to 4%w, of a phosphorus component calculated on the base of the phosphorus content. The catalyst can be used in any of a variety of shapes such as spheres and extrudates. The preferred shape is a trilobal extrudate. Preferably, the catalyst is sulphided prior to use, as is well known to the art.

The use of low-phosphorus or no-phosphorus catalysts in the second zone is thought to be of benefit due to reduced deactivation by coking.

Low-phosphorus content catalysts having high surface areas (greater than about 200 m²/g) and high compacted bulk densities (0.6-0.85 g/cm³) are preferably used for the second zone as they appear to be highly active. The high surface area increases reaction rates due to generally increased dispersion of the active components. Higher density catalysts allow one to load a larger amount of active metals and promoter per reactor volume, a factor which is commercially important. The metal content specified above provides high activity per reactor volume. Lower metal contents normally result in catalysts exerting two low activities for proper use in the process according to the present invention. Higher metal loadings than specified above do not contribute significantly to the performance and thus lead to an inefficient use of the metals resulting in high catalyst cost with little advantage. Since deposits of coke are thought to cause the majority of the catalyst deactivation, fresh catalyst pore volume should be at or above a modest level (0.4-0.8 cm³/g, more narrowly 0.5-0.7 cm³/g). The second zone catalyst can be used like the first zone catalyst in a variety of shapes. Preferably, the catalyst is sulphided prior to use as is well known to the art.

The Ni-containing catalyst used for the first zone is preferably a high activity conventional catalyst suitable for high

levels of hydrogenation. Such catalysts have high surface areas (greater than 140 m²/g) and high compacted bulk densities (0.65-0.95 g/cm³, more narrowly 0.7-0.95 g/cm³). The high surface area increases reaction rates due to generally increased dispersion of the active components. Higher density catalysts allow one to load a larger amount of active metals and promoter per reactor volume, a factor which is commercially important. The metal and phosphorus content specified above provides the high activity per reactor volume. Lower metal contents result in catalysts exerting too low activities for proper use in the process according to the present invention. Higher metal contents do not contribute significantly to the performance and thus lead to an insufficient use of the metals and higher cost for the catalyst. Since deposits of coke are thought to cause the majority of the catalyst deactivation, fresh catalyst pore volume should be at a modest level (0.4-0.8 cm³/g, more narrow 0.4-0.6 cm³/g).

A low-phosphorus or no-phosphorus conventional hydrotreating catalyst containing a carrier consisting essentially of alumina is used in the second zone of the catalyst system. Co and/or Ni containing conventional catalysts can be suitably applied. The second zone catalyst differs from the first zone catalyst primarily in its low-phosphorus content (less than 0.5%w). The catalyst contains less than 0.5%w phosphorus and comprises a component from group VIB and a group VIII metal or metal oxide, or metal sulphide and/or mixtures thereof composited with a support consisting essentially of alumina. Preferably, the catalyst comprises a nickel and/or cobalt component and a molybdenum and/or tungsten component with an alumina support. Preferred metal contents are up to 10%w, usually 1 to 5%w of group VIII metal component(s) calculated on the base of the metal content, and from 3 to 30%w of group VIB metal component (s) in the base of the metal content. A more preferred catalyst comprises a cobalt or nickel component and a molybdenum component with an alumina support.

The present invention preferably relates to a process for hydrotreating oils having a tendency to deactivate hydrotreating catalysts by coke formation, by passing a) oils having a final boiling point above 538°C and having less than 2%w of heptane asphaltenes, b) oils having a final boiling point from 343°C to 538°C, or c) mixtures thereof downwardly with hydrogen or a hydrogen-containing gas (mixture) into a hydrotreating zone over a stacked-bed of two hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to H₂S, wherein said stacked-bed comprises an upper zone containing of from 15-85%v, based on total catalyst, of a high-activity hydrotreating catalyst which comprises from 2-4%w nickel, from 8-15%w molybdenum and from 1-4%w phosphorus supported on a carrier consisting mostly of alumina, and a lower zone containing of from 15-85%v, basis total catalyst, of a high-activity, hydrodesulphurization catalyst which comprises from 2-4%w cobalt and/or nickel, from 8-15%w molybdenum and less than 0.5%w phosphorus supported on a carrier consisting essentially of alumina; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid oil having reduced sulphur and/or heavy metal content.

The physical characterizations of the catalysts referred to herein are common to those skilled in the catalyst development art. Surface areas refer to nitrogen adsorption surface areas preferably determined by at least three points. Pore size distributions are determined by mercury intrusion and calculated with a 130 degree contact angle. Pore volumes stated are water pore volumes and indicate the volume of water per weight of catalyst necessary to fill the catalyst pores to an incipient wetness of the catalyst.

The volume of the first catalyst zone in the present invention is from 15 to 85%v of the main catalyst charge. The remaining fraction of the main catalyst charge is composed of the second catalyst. The division of the catalyst volumes over the zones in the bed depends upon the requirement for nitrogen conversion versus the requirements for stability and other hydrotreating reactions such as sulphur and metals removal. Stacked-beds can be used to tailor the amount of nitrogen removal, sulphur and metals removal, and system stability. An increase in the first catalyst will increase the nitrogen removal but will effect the hydrodesulphurization (HDS) activity and stability of the system. Below a catalyst ratio of 15:85 or above a catalyst ratio of 85:15 (upper:lower) the benefits for the stacked-bed system are not large enough to be of practical significance. There is no physical limit on using a smaller percentage of one or the other beds.

The catalyst zones referred to herein may be in the same or different reactors. For existing units with one reactor the catalysts are layered one on top of the other. Many hydrotreating reactors consist of two or more reactors in series. The catalyst zones are not restricted to the particular volume of one vessel and can extend into the next (prior) vessel. The zones discussed herein refer to the main catalyst bed. Small layers of catalysts which are different sizes are frequently used in reactor loading as is known to those skilled in the art. Intervessel heat exchange and/or hydrogen addition may also be used in the process according to the present invention.

The pore size of the catalyst does not play a critical role in the process according to the present invention. The catalysts in the two zones may be based upon the same carrier. Normally, the finished catalysts will have small differences in their average pore sizes due to the differences in the respective metal and phosphorus loadings.

Suitable conditions for operating the catalyst system in accordance with the present invention are given in Table I.

TABLE I

Conditions	Broadest range	Broad range	Narrow range	Narrowest range
Hydrogen partial pressure, bar	6.8-75	20-75	20-55	34-55
Total pressure, bar	13.6-95	27-95	27-75	47-75
Hydrogen/feed ratio, NI/kg feed	17-1780	17-890	51-255	85-255
Temperature, °C	150-455	285-455	285-425	345-425
Liquid hourly space velocity, kg/kg · h	0.1-10.0	-	0.5-5.0	-

At temperatures below 285°C (for very heavy feeds) and below 150°C (for heavy feeds), the catalysts do not exhibit sufficient activity for the rates of conversion to be of practical significance. At temperatures above 455°C the rate of coking and cracking become excessive resulting in increasingly impractical operations. Reactor metallurgy may also be a limiting constraint above 455°C at the higher pressures.

At liquid space velocities below 0.1 kg/kg · h, the residence time of the oil is long enough to lead to thermal degradation and coking. At liquid space velocities above 10 kg/kg · h the conversion across the reactor is too small to be of practical use. For space velocity and gas-to-oil ratio calculations referred to herein, volumes are measured at 15.5°C and atmospheric pressure.

Hydrogen partial pressure is very important in determining the rate of catalyst coking and deactivation. At pressures below 6.8 bar, the catalyst system cokes too rapidly even with better quality oil containing high boiling components. At pressures above 75 bar, the deactivation mechanism of the catalyst system appears to be predominantly that of metals deposition, if present, which results in pore-mouth plugging. Catalysts of varying porosity can be used to address deactivation by metals deposition, as is known by those skilled in the art. The hydrogen to feed ratio to be applied in the process according to the present invention is required to be above 17 NI/kg feed since the reactions occurring during hydrotreating consume hydrogen, resulting in a deficiency of hydrogen at the bottom of the reactor. This deficiency may cause rapid coking of the catalyst and leads to impractical operation. At hydrogen to feed ratios in excess of 890 NI/kg feed, no substantial benefit is obtained; thus the expense of compression beyond this rate is not warranted.

Nitrogen removal is an important factor in hydrotreating heavy oils. Catalysts without phosphorus can be more stable with heavy oils under the conditions noted above; however, nitrogen removal activity is low for no-phosphorus catalysts relative to their phosphorus promoted counterparts. Additionally, Co promoted catalysts are less active for nitrogen removal than are Ni promoted catalysts. Stacked catalyst beds can be used to tailor the amount of nitrogen removal, sulphur and metals removal, and system stability. It has been found that a stacked-bed system also improves activities (other than nitrogen removal) as well as the stability of the overall catalyst system relative to either catalyst used individually. The stacked-bed catalyst system is applicable when processing feeds under conditions where a heavy feed is causing deactivation primarily by coking.

The process according to the present invention should be operated at conditions suitable to remove at least 25% and generally conditions will be applied to remove 30-80%, more preferably 45-75%, of the sulphur in the feed. When metals such as Ni and V are present in the feed and demetallization is the primary focus the process can be operated at the lower levels of desulphurization. When there is little metal in the feed and demetallization is not the primary goal, one can operate the process at higher sulphur removal rates.

The invention is accompanied by Figures 1 and 2 wherein some of the results as described in the Examples are depicted graphically.

Figure 1 represents a graph showing the advantage obtained in the reactor inlet temperature as a function of time when the stacked-bed according to the present invention is utilized.

Figure 2 represents a graph showing the advantage obtained in the reactor outlet temperature as a function of time when the stacked-bed according to the present invention is utilized.

The following Examples are presented to illustrate the present invention.

Example 1

A catalyst A containing nickel, molybdenum and phosphorus supported on a gamma alumina carrier was prepared from commercially available alumina powders. This carrier was extruded into 1.6 mm pellets having a trilobal cross section. The pellets were dried and calcined before being impregnated with the appropriate catalytically active metals

by a dry pore volume method i.e., by adding only enough solution to fill the alumina pore volume. Carriers containing in addition to alumina, a few per cent of other components like silica or magnesia can also be applied. An appropriate aqueous solution of nickel nitrate, nickel carbonate, phosphoric acid, hydrogen peroxide, and ammonium molybdate was used to impregnate the carrier. The metal loadings and some properties of the dried, calcined catalyst (A) are given in Table II.

A catalyst B containing cobalt and molybdenum supported on a similar alumina carrier as used to prepare catalyst A was prepared. Likewise, this carrier was also extruded into 1.6 mm pellets having a trilobal cross-section. The pellets were dried before being impregnated with the appropriate catalytically active metals by a dry pore volume method. An appropriate aqueous solution of cobalt carbonate, ammonium dimolybdate and ammonia was used to impregnate the carrier. The metal loadings and properties of the dried, calcined catalyst (B) are also given in Table II.

TABLE II

Catalyst	A	B
Diameter	1.6 mm	1.6 mm
Cross-section	Trilobal	Trilobal
Composition, %w		
Ni	3.0	-
Co	-	3.2
Mo	13.0	9.6
P	3.2	-
Compacted bulk density, g/cm ³	0.82	0.71
Surface Area, m ² /g	164	226
Hg-pore volume, cm ³ /g	0.47	0.61

Three different commercial runs with a main catalyst charge of a Ni-Mo-P/alumina catalyst, a Co-Mo/alumina catalyst and a stacked-bed of a Ni-Mo-P/alumina catalyst over a Co-Mo/alumina catalyst were carried out. In Fig. 1 the reactor inlet temperature (RIT in °C) necessary to maintain 0.3% weight sulphur in the product is graphically represented as a function of time (days), which is a convenient measure of general catalyst activity. The Ni-Mo-P catalyst data are represented as circles (upper line), the Co-Mo catalyst data as triangles (middle line) and the stacked catalyst data as diamonds (lower line). The stacked-bed system has good activity and stability for sulphur removal as well as denitrification advantages. The average feed properties and average unit conditions are given in Table III. The feed applied was a heavy vacuum gas oil having a final boiling point above 538°C and containing less than 2%w of heptane asphaltenes. Feed to the unit and unit conditions were remarkably constant during the runs considering the unit is a commercial unit. In the stacked-bed system the Ni-Mo-P catalyst formed about 33% of the main catalyst load while the Co-Mo catalyst made up the remainder of the main catalyst load. Oil and gas flowed in a single-stage and serially over first the Ni-Mo-P catalyst and then over the Co-Mo catalyst.

The main advantages of the stacked-bed system shown by this Example comprises a) a significant increase in catalyst stability as can be seen in Fig. 1 where the increase in RIT with time is significantly less for the stacked-bed system (3.1°C/month versus 12.5°C/month) relative to the single catalyst system; b) an increase in catalyst activity as represented by about a 8.1°C lower initial RIT for the same level of sulphur in the product; c) a resulting greatly improved estimated catalyst life of about 400% for the stacked-bed relative to the single bed due to the improvements in activity and stability. An end of run temperature of 416°C and a continued linear decline rate was used to estimate the catalyst life of the stacked-bed system.

TABLE III

Feed/process properties Hydrogen partial pressure 38 bar	
Liquid hourly space velocity	3 kg/kg · h
Sulphur, % wt	1.1
Nickel, ppm	0.6
Vanadium, ppm	0.7
RCR, %wt	0.3
TBP-GLC, °C	
IBP/10%	265/347
90/95%	524/538

Example 2

A second set of two commercial runs with a Ni-Mo-Plalumina catalyst and a stacked-bed of a Ni-Mo-Plalumina catalyst over a Co-Mo/alumina catalyst was also carried out. A Ni-Mo-P/alumina catalyst would be one that one skilled in the art would traditionally have chosen for this feedstock when considering hydrogenation, denitrification, and desulphurization catalyst activity rather than a Co-Mo catalyst. Table IV summarizes approximate average unit conditions and feedstock. The oil is a blend of straight run vacuum gas oil (distilled from non-cracked oil) and a coker heavy gas oil. In Table V the approximate average performance for the two runs at two catalyst ages is summarized and in Figure 2 the reactor outlet temperature necessary to maintain 0.75% weight and 0.60% weight sulphur in the product for the single catalyst and the stacked bed system is depicted as a function of time (days).

The main advantage of the stacked-bed system relative to the single bed system shown by this Example comprise a) higher sulphur conversion, even at lower operating temperatures, b) greater catalyst stability when processing the same type feed-about first 60 days-, c) processing a heavier feed at comparable stabilities-about after 60 days-, and d) greater hydrogen addition even at lower operating temperatures. It can be seen from Fig. 2 that the single bed system has a lower start of run temperature in the first one or two weeks but this temperature relates to 0.75%w sulphur in the product where the temperature for the stacked-bed system relates to 0.60%w sulphur in the product. To obtain also 0.6% weight sulphur in the product initially with the single bed system an additional 7.5°C would be required, thereby making the single bed about 4.4°C less active initially. It will be clear from Fig. 2 that although the two different catalyst configurations have similar temperatures at the start of run (for the different sulphur targets), the stacked-bed system has about a 12.5°C advantage after 2 months indicating the greater stability when processing the same type feed containing about 30% by volume of the coker material. After about 60 days the coking tendency of the feed to the single bed system was reduced by decreasing the amount of the full range coker heavy gas oil from about 30% down to 20% by volume (indicated by an arrow in the upper line of Fig. 2). The single bed system stability improved with the feed having reduced coking tendency and is beginning to approach that of the stacked-bed system although still at the higher sulphur in product level. This data shows that the stacked-bed system can be used to process a feed with greater coking tendency with equivalent catalysts life and for this case even with higher sulphur conversion. Table V provides some data indicating that the hydrogen consumption of the stacked-bed system is some 6% better (lower) than that of the single bed system. The best comparison is at the 1 month point where the catalysts are processing the same feed. The larger hydrogen consumption is reflected in the greater temperature rise across the reactor (Reactor delta T in Table V); hydrogen addition is a major factor in the heat release during hydrotreating.

TABLE IV

Feed properties and operating parameters	
Feed	Vacuum gas oil/coker heavy gas oil
Ratio	40/60
End Point, °C	above 538°C
Feed Sulphur, %w	~3
LHSV, kg/kg·h	2.76
H ₂ pressure (Reactor inlet) bar	49.3
H ₂ /oil ratio (NI/kg feed)	289

TABLE IV (continued)

Feed properties and operating parameters		
Feed	Vacuum gas oil/coker heavy gas oil	
Individual feedstocks	Vac. gas oil	Coker heavy gas oil
Molecular weight	369	312
Carbon, %w	85.4	85.2
Hydrogen, %w	11.8	11.0
Sulphur, %w	2.5	3.2
TBP-GLC wt 538°C	91.2	95.0

TABLE V

Catalysts and performance				
Catalyst age	1 month		4 months	
Catalyst*	1	1 & 2	1	1 & 2
Reactor temp., out, °C	360	357.2	376.7	362.8
Reactor delta T, °C	37.5	40.6	34.4	40.6
H ₂ consumption, NI/kg feed	63.8	68	63.8	68
Product sulphur, %w	0.75	0.6	0.75	0.6

*Catalyst 1 is Ni-Mo-P
Catalyst 2 is Co-Mo

Example 3

A third set of two commercial runs with a Ni-Mo-Plalumina catalyst and a stacked-bed of a Ni-Mo-Plalumina catalyst and a Co-Mo/alumina catalyst was also made. The feed used has a final boiling point between 343°C and 538°C and contained straight run light gas oil, coker naphtha, coker light gas oil and light cycle oil. In Table VI the approximate average unit conditions and feed stock properties are summarized. Analysis of the data for these two runs showed that the stacked-bed used in accordance with the present instant invention showed the following advantages when compared to the single catalyst:

- a) lower inlet temperature,
- b) lower sulphur in the product, and
- c) the ability to operate at the same reactor delta temperature even though the reactor inlet temperature was lower.

TABLE VI

Feed properties and operating parameter	
Feed gravity	0.92
Distillation, °C, end point	455
Feed sulphur, %w	1.3
Liquid hourly space velocity kg/kg · h	2.6
H ₂ pressure (reactor inlet, bar)	35.4
H ₂ /oil ratio, NI/kg feed	168.3

Claims

1. A process for catalytically hydrotreating hydrocarbon oils at elevated temperature and pressure in the presence of hydrogen in a hydrotreating zone over a stacked-bed of hydrotreating catalysts, characterized in that,

- a) oils having a final boiling point greater than 538 °C and containing less than 2 %w of heptane asphaltenes,
 b) oils having a final boiling point from 343 °C to 538 °C, or
 c) mixtures thereof,

are passed downwardly with hydrogen or a hydrogen-containing gas under conditions suitable to convert more than 25% of the sulphur compounds present to hydrogen sulphide at a hydrogen partial pressure of between 6.8 and 75 bar, wherein said stacked-bed comprises an upper zone containing 15-85 %v, based on total catalyst, of a hydrotreating catalyst comprising a component from Group VIB of the Periodic Table, a Group VIII metal or metal oxide or metal sulphide and a phosphorus oxide and/or sulphide in an amount of 1 to 10 %w calculated basis phosphorus content, and a lower zone containing 15-85 %v, based on total catalyst, of a hydrotreating catalyst comprising a component from Group VIB, a Group VIII metal or metal oxide or metal sulphide and less than 0.5 %w of phosphorus supported on a carrier consisting essentially of alumina, and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having a reduced heteroatom content.

2. A process according to claim 1, wherein a stacked-bed is used containing an upper zone containing up to 10 %w of a Group VIII component, 3-15 %w of a Group VIB component and 1-10 %w of phosphorus, and a lower zone containing up to 10 %w of a Group VIII component and 3-30 %w of a Group VIB component.

3. A process according to claim 1 or 2, wherein a stacked-bed is used containing an upper zone comprising a nickel component, a molybdenum and/or tungsten component and phosphorus on an alumina support which may additionally contain silica, and a lower zone comprising a nickel and/or cobalt component and a molybdenum and/or tungsten component on an alumina support.

4. A process according to claim 3, wherein a stacked-bed is used containing an upper zone containing 2-4 %w of nickel, 8-15 %w of molybdenum and 1-4 %w of phosphorus supported on a carrier consisting mostly of gamma alumina, and a lower zone containing 2-4 %w of cobalt, from 8-15 %w of molybdenum and less than 0.5 %w of phosphorus supported on a carrier consisting essentially of alumina.

5. A process according to any of claims 1-4, wherein a stacked-bed is used wherein the upper zone catalyst has a compacted bulk density of 0.65-0.95 g/cm³, in particular 0.76-0.88 g/cm³ and a surface area greater than 140 m²/g, in particular greater than 150 m²/g, and wherein the lower zone catalyst has a compacted bulk density of 0.6-0.8 g/cm³, in particular 0.67-0.69 g/cm³ and a surface area greater than 180 m²/g, in particular greater than 200 m²/g.

6. A process according to any one of claims 1-5, wherein use is made of a stacked-bed catalyst containing in its lower zone 2-4 %w of cobalt and essentially no nickel and no phosphorus.

7. A process according to any one of claims 1-5, wherein use is made of a stacked-bed catalyst containing in its lower zone 2-4 %w of nickel and essentially no cobalt and no phosphorus.

8. A process according to any one of claims 1-7, wherein use is made of a stacked-bed containing a trilobally shaped catalyst in the upper and/or the lower zone.

9. A process according to claim 8, wherein use is made of a catalyst carrier extruded into a trilobal shape before impregnation.

10. A process according to any one of claims 1-9, wherein the hydrotreating zone is contained in a single reactor and the upper zone of the stacked-bed catalyst comprises about one-third of the total catalyst volume.

11. A process according to any one of claims 1-10, wherein hydrocarbon oils having a tendency to deactivate hydrotreating catalysts by coke formation are hydrotreated by passing:

- a) oils having a final boiling point above 538 °C and having less than 2 %w of heptane asphaltenes,

- b) oils having a final boiling point from 343 °C to 538 °C, or
- c) mixtures thereof,

downwardly with hydrogen or a hydrogen-containing gas into a hydrotreating zone over a stacked-bed of two hydrotreating catalysts under conditions suitable to convert more than 25% of the sulphur compounds present to H_2S at a hydrogen partial pressure of between 6.8 and 75 bar; said stacked-bed comprising an upper zone containing of from 15-85 %v, based on total catalyst, of a high-activity hydrotreating catalyst which comprises from 2-4 %w nickel, from 8-15 %w molybdenum and from 1-4 %w phosphorus supported on a carrier consisting mostly of alumina, said catalyst having a compacted bulk density of 0.65-0.95 g/cm³ and a surface area greater than 140 m²/g; and a lower zone containing from 15-85 %v, based on total catalyst, of a high-activity, hydrosulphurization catalyst which comprises from 2-4 %w cobalt and/or nickel and from 8-15 %w molybdenum and less than 0.5 %w phosphorus supported on a carrier consisting essentially of alumina, said catalyst having a compacted bulk density of 0.6-0.8 g/cm³ and a surface area greater than 180 m²/g; and separating the reaction product from said hydrotreating zone into a hydrogen-rich gas and a liquid hydrocarbon oil having reduced sulphur content.

Patentansprüche

1. Ein Verfahren zur katalytischen Hydrobehandlung von Kohlenwasserstoffölen bei erhöhter Temperatur und erhöhtem Druck in Gegenwart von Wasserstoff in einer Hydrobehandlungszone über einem Schichtbett aus Hydrobehandlungskatalysatoren, dadurch **gekennzeichnet**, daß

- a) Öle mit einem Endsiedepunkt von mehr als 538°C und mit einem Gehalt von weniger als 2 Gew.% Heptan-asphaltenen,
- b) Öle mit einem Endsiedepunkt von 343°C bis 538°C oder
- c) Mischungen davon

zusammen mit Wasserstoff oder einem Wasserstoff enthaltenden Gas unter für die Umwandlung von mehr als 25% der vorhandenen Schwefelverbindungen in Schwefelwasserstoff geeigneten Bedingungen bei einem Wasserstoffpartialdruck zwischen 6,8 und 75 bar durch das Bett in Abwärtsrichtung geleitet werden, wobei das genannte Schichtbett eine obere Zone, enthaltend 15 bis 85 Volumenprozent, bezogen auf den Gesamtkatalysator, eines Hydrobehandlungskatalysators, umfassend eine Komponente aus der Gruppe VIB des Periodischen Systems der Elemente, ein Metall, Metalloxid oder Metallsulfid der Gruppe VIII und ein Phosphoroxid und/oder -sulfid in einer Menge von 1 bis 10 Gew.%, bezogen auf den Phosphorgehalt, und eine untere Zone, enthaltend 15 bis 85 Volumenprozent, bezogen auf den Gesamtkatalysator, eines Hydrobehandlungskatalysators, umfassend eine Komponente der Gruppe VIB, ein Metall, Metalloxid oder Metallsulfid der Gruppe VIII und weniger als 0,5 Gew.% Phosphor, aufgebracht auf einen Träger, der im wesentlichen aus Aluminiumoxid besteht, umfaßt; und das Reaktionsprodukt aus der genannten Hydrobehandlungszone in ein wasserstoffreiches Gas und ein flüssiges Kohlenwasserstofföl mit reduziertem Heteroatomgehalt aufgetrennt wird.

2. Ein Verfahren nach Anspruch 1, in welchem ein Schichtbett, umfassend eine obere Zone, enthaltend bis zu 10 Gew.% einer Komponente der Gruppe VIII, 3 bis 15 Gew.% einer Komponente der Gruppe VIB und 0,1 bis 10 Gew.% Phosphor, und eine untere Zone, enthaltend bis zu 10 Gew.% einer Komponente der Gruppe VIII und 3 bis 30 Gew.% einer Komponente der Gruppe VIB, verwendet wird.
3. Ein Verfahren nach Anspruch 1 oder 2, in welchem ein Schichtbett, umfassend eine obere Zone, enthaltend eine Nickelkomponente, eine Molybdän- und/oder Wolframkomponente und Phosphor auf einem Aluminiumoxidträger, welcher zusätzlich Siliciumdioxid enthalten kann, und eine untere Zone, enthaltend eine Nickel- und/oder Kobaltkomponente und eine Molybdän- und/oder Wolframkomponente auf einem Aluminiumoxidträger, verwendet wird.
4. Ein Verfahren nach Anspruch 3, in welchem ein Schichtbett, umfassend eine obere Zone, enthaltend 2 bis 4 Gew.% Nickel, 8 bis 15 Gew.% Molybdän und 1 bis 4 Gew.% Phosphor auf einem Träger, welcher im wesentlichen aus gamma-Aluminiumoxid besteht, und eine untere Zone, enthaltend 2 bis 4 Gew.% Kobalt, 8 bis 15 Gew.% Molybdän und weniger als 0,5 Gew.% Phosphor auf einem Träger, der im wesentlichen aus Aluminiumoxid besteht, verwendet wird.
5. Ein Verfahren nach einem der Ansprüche 1 bis 4, in welchem ein Schichtbett verwendet wird, bei dem der Katalysator der oberen Zone eine Schüttdichte im verdichteten Zustand von 0,65 bis 0,95 g/cm³, vorzugsweise von

0,76 bis 0,88 g/cm³ und eine Oberflächenausdehnung von mehr als 140 m²/g, vorzugsweise von mehr als 150 m²/g, und der Katalysator der unteren Zone eine Schüttdichte im verdichteten Zustand von 0,6 bis 0,8 g/cm³, vorzugsweise von 0,67 bis 0,69 g/cm³ und eine Oberflächenausdehnung von mehr als 180 g/m², vorzugsweise von mehr als 200 m²/g, aufweist.

- 5 6. Ein Verfahren nach einem der Ansprüche 1 bis 5, in welchem ein Schichtbettkatalysator eingesetzt wird, welcher in seiner unteren Zone 2 bis 4 Gew.% Kobalt und im wesentlichen kein Nickel und keinen Phosphor enthält.
- 10 7. Ein Verfahren nach einem der Ansprüche 1 bis 5, in welchem ein Schichtbettkatalysator eingesetzt wird, der in seiner unteren Zone 2 bis 4 Gew.% Nickel und im wesentlichen kein Kobalt und keinen Phosphor enthält.
8. Ein Verfahren nach einem der Ansprüche 1 bis 7, in welchem ein Schichtbett verwendet wird, das einen dreilappig geformten Katalysator in der oberen und/oder unteren Zone enthält.
- 15 9. Ein Verfahren nach Anspruch 8, in welchem ein Katalysatorträger eingesetzt wird, der vor dem Imprägnieren in dreilappiger Form extrudiert worden ist.
10. Ein Verfahren nach einem der Ansprüche 1 bis 9, in welchem die Hydrobehandlungszone in einem einzigen Reaktor enthalten ist und die obere Zone des Schichtbettes ca. 1/3 des gesamten Katalysatorvolumens ausmacht.
- 20 11. Ein Verfahren nach einem der Ansprüche 1 bis 10, in welchem Kohlenwasserstofföle mit einer Neigung, Hydrobehandlungskatalysatoren unter Bildung von Koks zu deaktivieren, durch die folgenden Schritte hydrobehandelt werden:
 - 25 a) Öle mit einem Endsiedepunkt von mehr als 538°C und einem Gehalt von weniger als 2 Gew.% Heptanasphaltenen,
 - b) Öle mit einem Endsiedepunkt von 343°C bis 538°C, oder
 - c) Mischungen davon

30 werden mit Wasserstoff oder einem wasserstoffhaltigen Gas in einer Hydrobehandlungszone in Abwärtsrichtung über ein Schichtbett aus zwei Hydrobehandlungskatalysatoren bei für die Umwandlung von mehr als 25% der vorhandenen Schwefelverbindungen in H₂S geeigneten Bedingungen und bei einem Wasserstoffpartialdruck zwischen 6,8 und 75 bar geleitet; das genannte Schichtbett enthält eine obere Zone, enthaltend von 15 bis 85 Volumenprozent, bezogen auf den Gesamtkatalysator, eines hochaktiven Hydrobehandlungskatalysators, welcher 2 bis 4 Gew.% Nickel, 8 bis 15 Gew.% Molybdän und 1 bis 4 Gew.% Phosphor auf einem Träger, der im wesentlichen aus Aluminiumoxid besteht, enthält, wobei dieser Katalysator eine Schüttdichte im verdichteten Zustand von 0,65 bis 0,95 g/cm³ und eine Oberflächenausdehnung von mehr als 140 m²/g aufweist; und eine untere Zone, enthaltend 15 bis 85 Volumenprozent, bezogen auf den Gesamtkatalysator, eines hochaktiven Hydroentschwefelungskatalysators, welcher 2 bis 4 Gew.% Kobalt und/oder Nickel und 8 bis 15 Gew.% Molybdän und weniger als 0,5 Gew.% Phosphor auf einem Träger, der zum größten Teil aus Aluminiumoxid besteht, enthält, wobei dieser Katalysator eine Schüttdichte im verdichteten Zustand von 0,6 bis 0,8 g/cm³ und eine Oberflächenausdehnung von mehr als 180 m²/g aufweist; und dann wird das Reaktionsprodukt aus der genannten Hydrobehandlungszone in ein wasserstoffreiches Gas und ein flüssiges Kohlenwasserstofföl mit reduziertem Schwefelgehalt aufgetrennt.

45 Revendications

1. Procédé d'hydrotraitement catalytique d'huiles hydrocarbonées à température et pression élevées en présence d'hydrogène dans une zone d'hydrotraitement sur un lit empilé de catalyseurs d'hydrotraitement, caractérisé en ce que l'on fait passer de haut en bas
 - 50 a) des huiles possédant un point d'ébullition supérieur à 538°C et contenant moins de 2 % en poids d'asphaltenes insolubles dans l'heptane,
 - b) des huiles possédant un point d'ébullition final de 343°C à 538°C, ou
 - 55 c) des mélanges de ces huiles,

avec de l'hydrogène, ou un gaz contenant de l'hydrogène, dans des conditions convenant à convertir plus de 25 % des composés du soufre présents en hydrogène sulfuré, à une pression partielle d'hydrogène comprise entre

- 6,8 et 75 bars, où le lit empilé précité comprend une zone supérieure contenant 15 à 85 % en volume, sur base du catalyseur total, d'un catalyseur d'hydrotraitement comprenant un composant du Groupe VIB du Tableau Périodique, un métal du Groupe VIII, ou un oxyde de métal, ou un sulfure de métal du Groupe VIII et un oxyde de phosphore et/ou un sulfure de phosphore en une proportion de 1 à 10 % en poids, calculés sur base de la teneur en phosphore, et une zone inférieure contenant de 15 à 85 % en volume, sur base du catalyseur total, d'un catalyseur d'hydrotraitement comprenant un composant du Groupe VIB, un métal du Groupe VIII, ou un oxyde de métal ou un sulfure de métal du Groupe VIII et moins de 0,5 % en poids de phosphore, sur un support ou véhicule essentiellement constitué d'alumine, et on sépare le produit de la réaction sortant de ladite zone d'hydrotraitement en un gaz riche en hydrogène et une huile hydrocarbonée liquide possédant une teneur réduite en hétéro-atomes.
2. Procédé suivant la revendication 1, caractérisé en ce que l'on utilise un lit empilé contenant une zone supérieure contenant jusqu'à 10 % en poids d'un composant du Groupe VIII, 3 à 15 % en poids d'un composant du Groupe VIB et 1 à 10 % en poids de phosphore et une zone inférieure contenant jusqu'à 10 % en poids d'un composant du Groupe VIII et 3 à 30 % en poids d'un composant du Groupe VIB.
 3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que l'on utilise un lit empilé contenant une zone supérieure comprenant un composant de nickel, un composant de molybdène et/ou de tungstène et du phosphore sur un support d'alumine, qui peut en outre contenir de la silice, et une zone inférieure comprenant un composant de nickel et/ou de cobalt et un composant de molybdène et/ou de tungstène sur un support d'alumine.
 4. Procédé suivant la revendication 3, caractérisé en ce que l'on utilise un lit empilé contenant une zone supérieure contenant 2 à 4 % en poids de nickel, 8 à 15 % en poids de molybdène et 1 à 4 % en poids de phosphore sur un support ou véhicule constitué principalement de gamma-alumine, et une zone inférieure contenant 2 à 4 % en poids de cobalt, de 8 à 15 % en poids de molybdène et moins de 0,5 % en poids de phosphore sur un support ou véhicule essentiellement constitué d'alumine.
 5. Procédé suivant l'une quelconque des revendications 1 à 4, caractérisé en ce que l'on utilise un lit empilé dans lequel le catalyseur de la zone supérieure possède une masse volumique apparente à l'état tassé de 0,65 à 0,95 g/cm³, plus particulièrement, de 0,76 à 0,88 g/cm³ et une surface spécifique supérieure à 140 m²/g, plus particulièrement, supérieure à 150 m²/g, et dans lequel le catalyseur de la zone inférieure possède une masse volumique apparente à l'état tassé de 0,6 à 0,8 g/cm³, plus particulièrement, de 0,67 à 0,69 g/cm³ et une surface spécifique supérieure à 180 m²/g, plus particulièrement, supérieure à 200 m²/g.
 6. Procédé suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que l'on utilise un catalyseur à lit empilé contenant, dans sa zone inférieure, 2 à 4 % en poids de cobalt et sensiblement ni nickel, ni phosphore.
 7. Procédé suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que l'on utilise un catalyseur à lit empilé contenant, dans sa zone inférieure, 2 à 4 % en poids de nickel et sensiblement ni cobalt, ni phosphore.
 8. Procédé suivant l'une quelconque des revendications 1 à 7, caractérisé en ce que l'on utilise un lit empilé contenant un catalyseur de forme trilobée dans la zone supérieure et/ou la zone inférieure.
 9. Procédé suivant la revendication 8, caractérisé en ce que l'on utilise un véhicule ou support de catalyseur extrudé en une forme trilobée avant l'imprégnation.
 10. Procédé suivant l'une quelconque des revendications 1 à 9, caractérisé en ce que la zone d'hydrotraitement est contenue dans un réacteur unique et la zone supérieure du catalyseur à lit empilé constitue environ un tiers du volume total du catalyseur.
 11. Procédé suivant l'une quelconque des revendications 1 à 10, caractérisé en ce que l'on soumet à un hydrotraitement des huiles hydrocarbonées qui ont tendance à désactiver des catalyseurs d'hydrotraitement par formation de coke, en faisant passer de haut en bas :
 - a) des huiles possédant un point d'ébullition final supérieur à 538°C et possédant moins de 2 % en poids d'asphaltènes insolubles dans l'heptane,
 - b) des huiles possédant un point d'ébullition final de 343 à 538°C, ou
 - c) des mélanges de ces huiles,

avec de l'hydrogène, ou un gaz contenant de l'hydrogène, dans une zone d'hydrotraitement sur un lit empilé de deux catalyseurs d'hydrotraitement dans des conditions convenant à convertir plus de 25 % des composés du soufre présents en H_2S , à une pression partielle d'hydrogène comprise entre 6,8 et 75 bars, le lit empilé précité comprenant une zone supérieure contenant de 15 à 85 % en volume, sur base du catalyseur total, d'un catalyseur d'hydrotraitement à haute activité, qui comprend de 2 à 4 % en poids de nickel, de 8 à 15 % en poids de molybdène et de 1 à 4 % en poids de phosphore, sur un support ou véhicule constitué principalement d'alumine, ledit catalyseur possédant une masse volumique apparente à l'état tassé de 0,65 à 0,95 g/cm³ et une surface spécifique supérieure à 140 m²/g, et une zone inférieure contenant de 15 à 85 % en volume, sur base du catalyseur total, d'un catalyseur d'hydrodésulfuration à haute activité, qui comprend de 2 à 4 % en poids de cobalt et/ou de nickel et de 8 à 15 % en poids de molybdène et moins de 0,5 % en poids de phosphore, sur un support ou véhicule essentiellement constitué d'alumine, le catalyseur en question possédant une masse volumique apparente à l'état tassé de 0,6 à 0,8 g/cm³ et une surface spécifique supérieure à 180 m²/g et on sépare le produit de la réaction sortant de ladite zone d'hydrotraitement en un gaz riche en hydrogène et en une huile hydrocarbonée liquide possédant une teneur réduite en soufre.

